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NOTES ON ORGANIC ANALYSIS.

BY HENRY C. SHERMAN.

The purpose of these articles is to give a connected view of organic analysis as applied to plant and animal substances and their manufactured products. No attempt is made to touch upon all branches of this subject but certain important elements and compounds are treated in considerable detail and so far as possible in systematic order, the methods described being such as are applicable to the cases most likely to be met in practical work.

After an introductory chapter the following subjects will be taken up: The determination of nitrogen, sulphur and phosphorus; the analytical chemistry and quantitative determination of typical alcohols, aldehydes, carbohydrates (including the analysis of raw sugar and commercial glucose), organic acids, fats, commercial oils, soaps, the more important nitrogenous compounds of plant and animal substances; and finally the analysis of complex food materials such as cereals, cocoa, meat and milk. As a rule coal tar and petroleum products and purely synthetic preparations are considered only in so far as they occur in mixtures which are primarily of animal or vegetable origin.

References to books and journal articles will be given in each chapter and the notes will be concluded with an appendix containing similar references for important subjects not covered by the text.

These notes were written primarily for the use of students in organic and sanitary analysis at Columbia University. With

Mason's *Examination of Water* and Richards and Woodman's *Air, Water and Food*, they cover the work of the course in this subject which is required of third year students in the School of Chemistry and a part of that offered to graduate students in the School of Pure Science. A knowledge of inorganic quantitative analysis and of elementary organic chemistry is, therefore, presupposed.

CHAPTER I.

Introduction.

ULTIMATE AND PROXIMATE ANALYSIS.

Ultimate organic analysis is the determination of the elements composing any organic substance. Proximate organic analysis is the determination of the compounds present in a mixture, or of the radicals present in a compound.

Both ultimate and proximate analyses are often required in the examination of organic materials. In the case of a complex mixture, however, proximate analysis is frequently directed to the determination of the principal groups of related compounds rather than of each individual compound present.

In the analysis of ordinary animal and vegetable substances it is usually assumed that all of the organic matter is made up of not more than six elements — carbon, hydrogen, nitrogen, oxygen, sulphur and phosphorus. Other elements present would usually be found in the ash, though not always without loss as will be explained later.

While the results of ultimate analysis are often calculated to the basis of dry, ash-free substance, it is not to be supposed that the ash like the moisture is simply mixed with the organic matter of the original sample. In many cases the inorganic compounds found in the ash are formed during combustion, the bases having existed in combination with organic acids or proteids while the acid radicles may also have existed in organic combination or may have been formed by the oxidation of the carbon, sulphur and phosphorus of the organic matter.

The preliminary treatment of samples and the most generally applicable methods of ultimate analysis including the preparation and analysis of ash, will be briefly outlined in this chapter. In the one following, those methods which are more particularly adapted to the determination of nitrogen, sulphur and phosphorus in animal and vegetable substances will be more fully described.

PRELIMINARY TREATMENT OF SAMPLES.

Samples received and analyzed in liquid form should be kept in well-filled tightly-stoppered bottles and so far as possible in a cool

dark place. If the liquid already contains an antiseptic or is rich in any such preservative substance as salt, glycerol or alcohol, or if it can be kept at a sufficiently low temperature, no further precautions regarding the preservation of the sample will be required.

When there is danger of fermentation the sample should either be sterilized by heat or preserved by freezing or by the addition of an antiseptic, the latter method being usually the most practical. The choice of antiseptic will depend upon the nature of the sample and of the analysis to be made. Mercuric chloride, hydrogen peroxide, formaldehyde, salicylic acid, chloroform and thymol are among the most useful preservatives. Formaldehyde added in the proportion of 0.2 to 0.3 c.c. of the commercial forty per cent. solution to each 100 c.c. of sample is especially convenient and efficient but cannot be used in all cases as it may interfere with some of the tests to be made in the course of the analysis.

No fixed rules can be given for the preliminary treatment of solid samples but the following directions will apply in most cases.

If the sample is moist, dry it thoroughly in a boiling water oven, allow to cool in the air, note the loss in weight and use this "air-dry" sample for analysis. Always determine moisture in the air-dry sample so that the analytical results can be calculated to the "water-free" basis if desired.

An ordinary drug or coffee mill * is usually better than a mortar for grinding the air-dry sample. For proximate analysis of plant or animal tissues the preliminary grinding should theoretically be so thorough as to break all of the cells. In most cases it is found sufficient to grind until the sample passes a sieve having holes one-half millimeter in diameter.

Substances too tough or sticky to be ground by ordinary means can often be prepared by rasping or by grinding in a mortar with a known proportion of sharp sand or broken glass.

OUTLINE OF ULTIMATE ORGANIC ANALYSIS.

Ultimate organic analysis is discussed in so many well-known laboratory manuals that no attempt will be made to include the subject here. For comparison with the methods to be given in

* For laboratories where many fibrous samples are to be ground the Dreef mill is very advantageous. A description of this and other special forms of grinding apparatus will be found in Wiley's Agricultural Analysis, Volume III, Part First. (Easton, Pa., 1897).

the next chapter, however, the most generally applicable processes will be mentioned with references to some of the more complete or recent descriptions.

In the determination of carbon and hydrogen the sample is usually burned in a combustion tube in a current of air or oxygen, the products of combustion being led over hot copper oxide to ensure complete oxidation. The resulting water and carbon dioxide are absorbed respectively, either by calcium chloride and potassium hydroxide or by sulphuric acid and soda-lime. This method requires modification when the sample contains halogens, light metals, or considerable amounts of nitrogen or sulphur. For a discussion of such modifications as well as for the essential details of the process, the works of Benedict,* Hans Meyer † and Lassar-Cohn ‡ as well as older standard works should be consulted.

For the determination of nitrogen the Dumas method alone is applicable to all organic compounds. The substance is burned with copper oxide and the products of combustion passed over hot metallic copper. The nitrogen gas thus obtained is measured and its weight calculated. For details of this method see Gattermann,§ Hans Meyer (*l. c.*), or the methods of the Association of Official Agricultural Chemists. ||

For the determination of sulphur and phosphorus, the well-known method of Carius is considered the most generally applicable. The substance is oxidized by heating with fuming nitric acid in a sealed tube and the resulting sulphuric and phosphoric acids are determined by the usual methods. The manipulation of the Carius method is fully described by Gattermann.

Ultimate analyses can also be made by burning the substance with an excess of oxygen in a closed chamber such as the bomb used for calorimetric work or a specially constructed small autoclave. This method, proposed by Berthelot ¶ and developed largely by Hempel,** has been used extensively in fuel analyses by Lang-

* Elementary Organic Analysis, Easton, Pa., 1900.

† Analyse and Konstitutionsermittlung organischer Verbindungen, Berlin, 1903.

‡ Arbeitsmethoden für Organisch-chemische Laboratorien [3 Aufl.], Hamburg, 1903.

§ Practical Methods of Organic Chemistry, New York, 1901.

|| Bulletin 46, Bureau of Chemistry, U. S. Department of Agriculture.

¶ *Compt. rend.*, 1892, 114, 318; 1899, 129, 1002; *Ztschr. anal. Chem.*, 1901 40, 124.

** *Ber. deut. chem. Ges.*, 1897, 30, 202.

bein.* Its application to the determination of sulphur is given in the next chapter.

PREPARATION AND ANALYSIS OF ASH.

Preparation of Ash.

Incineration of ordinary substances is best accomplished in a flat platinum dish in a muffle. The substance should first be carefully charred at the front of the muffle, then burned until white or very light gray at a temperature of 500° to 600°.† If the temperature cannot be accurately known, the operation should be carefully watched and the dish never heated above a very low redness. Higher temperatures not only increase the loss of chlorides but may cause the ash to fuse over some of the carbon and thus greatly retard its combustion. If the substance is rich in salts of the alkalies, char it gently, extract with warm water, pour off the aqueous extract and set aside while burning the carbonaceous residue to whiteness, then return the aqueous extract to the platinum dish, evaporate to dryness, and ignite gently as already directed. Animal substances, seeds, and other samples rich in phosphates should be extracted with acetic acid instead of with water alone.

Various forms of special apparatus for the preparation of ash have been described, those of Shuttleworth,‡ Tucker§ and Wislicenus ‖ being probably the best known.

In order to avoid discrepancies due to the absorption of moisture from the air, the ash may be thoroughly mixed while still warm and transferred at once to a tightly stoppered weighing bottle. The ash being then perfectly dry, no determination of moisture is necessary and the portions required for analysis may be weighed out by difference.

Methods of Ash Analysis.

Since almost any of the elements found in soil or water may also be found in ash, no attempt to outline a complete scheme of

* *Ztschr. angew. Chem.*, 1900, 1227, 1259; 1901, 516.

† In a series of experiments by Thompson and the writer in which portions of dried milk were incinerated at known temperatures in an electrically heated muffle, it was found that increase of temperature from 450° to 600° had no appreciable influence upon the amount of chlorine recovered in the ash, but that a loss occurred at about 650°. For other results of this study see the chapter on milk analysis.

‡ Dissertation, Goettingen, 1899. *Journ. Landw.*, 1899, 47, 173.

§ *Ber. deut. chem. Ges.*, 1899, 32, 2583.

‖ *Ztschr. anal. Chem.*, 1901, 40, 441.

analysis would be of much practical use, especially since the amount of ash available is generally so small that the analysis must be limited to the determination of the more important constituents. The determinations most often required may be carried out in accordance with the plan adopted by the Association of Official Agricultural Chemists (*l. c.*). Methods of ash analysis are also described in Fresenius' *Quantitative Analysis* and in a paper by Tollens in the *Experiment Station Record*, Volume XIII., pages 207–220. For detailed descriptions of the separations and determinations required, text books on inorganic quantitative analysis * should be consulted. Small amounts of iron may conveniently be estimated by colorimetric methods.†

Interpretation of Ash Analysis.

Chlorine. — Even when the incineration has been carried on carefully at temperatures considerably below those at which the chlorides begin to volatilize, the whole of the chlorine of the original substance is rarely recovered in the ash.‡ Apparently this loss of chlorine is due to the formation of acid products in the early stages of ignition of the organic matter, when the conditions approach those of dry distillation. When the relative amount of organic matter is large these acid products are formed in such quantity as to expel a considerable part of the chlorine from its combination with the alkalies. The alkali thus retained in combination with organic matter is converted to carbonate by further ignition, and this in turn may be acted upon by some stronger acid formed during the combustion. The loss of chlorine increases with the proportion of organic matter to chloride. According to Davis § it may be prevented by the addition of sodium carbonate to the extent of 5 per cent. of the weight of organic matter present, but this of course is not permissible in the preparation of ash for general

* Among the more recent are — Classen: Ausgewählte Methoden der Analytischen Chemie, Braunschweig, 1901–1903. Treadwell: Analytical Chemistry, Vol. II. (Quantitative Analysis), New York, 1904. Miller: Quantitative Analysis for Mining Engineers, New York, 1904.

† Thompson: *Journ. Chem. Soc.*, 1885, 47, 493. Borntträger: *Chem. Ztg.*, 1896, 20, 398. Richards and Woodman: Air, Water and Food, New York, 1904. Pulsifer: *Journ. Amer. Chem. Soc.*, 1904, 26, 967.

‡ For a very full discussion of the loss of chlorine in the preparation of ash, including references to earlier work see Adlerskron: *Ztschr. anal. Chem.*, 1873, 12, 390.

§ *Journ. Soc. Chem. Ind.*, 1901, 20, 98.

analysis. Shuttleworth * recommends calcium acetate as being efficient in preventing loss of chlorine and especially convenient in the incineration of siliceous substances such as straw.

Carbonates. — Carbonates in ash are not derived necessarily from salts of carbonic or organic acids existing in the original substance. The bases found as carbonates in the ash may have been combined with proteids or may have been derived from inorganic salts decomposed by heating in contact with the large excess of organic matter, as just mentioned in the case of alkaline chlorides. On the other hand, carbonates originally present or formed during ignition may be changed to sulphates or phosphates by the action of acids resulting from the oxidation of organic sulphur or phosphorus.

Sulphates. — The amount of sulphate found in the ash bears little relation either to the total sulphur, or to that existing as sulphate in the original substance. Depending upon the other constituents present and the conditions of incineration, sulphates may be reduced or converted to phosphates, or, on the other hand, the organic sulphur may be largely oxidized and retained as sulphate. Very rarely in the combustion of natural products does all of the sulphur remain in the ash. More frequently only a small fraction of it is thus retained.

Phosphates. — The phosphates of the ash usually represent the whole of the pre-existing inorganic phosphates and, in the case of natural substances, usually much of the phosphorus which was present in organic combination. Since the latter exists mainly, if not entirely, as organic phosphates or substituted phosphoric acid, it is largely burned to free orthophosphoric acid and thus remains as mineral phosphate in the ash. With many substances, practically all of the phosphorus is thus retained as phosphate by the ash, but it cannot be assumed that such will be the case whenever there are bases enough to combine with all of the phosphoric acid. Thus there is some loss of phosphorus in burning the dried residue of milk at 600°, although the ash thus obtained contains a considerable proportion of chlorides. When the phosphoric acid formed is more than sufficient to saturate the bases present, the excess of acid is very slowly volatilized. In such cases the ash is apt to fuse over the last portions of unburned carbon, interfering both with the determination or preparation of ash and with the determination of carbon in the elementary analysis.

* Dissertation, Goettingen, 1899.

Bases. — Some of the heavy metals, if present, may be reduced and volatilized during the combustion of the organic matter. There is danger of mechanical loss of ash if combustion is carried on rapidly or in too strong a current of air. A sufficient circulation of air will be secured by inclining slightly the muffle in which the substance is burned. The volatilization of alkaline chlorides as such at temperatures of 650° or over has already been mentioned.

When small amounts of metallic bases are to be determined it is usually advantageous and often necessary to destroy the organic matter, in part at least, by boiling with acids instead of by burning in the air.*

* Neumann: *Ztschr. physiol. Chem.*, 1902–3, 37, 115. Meilliere: *Journ. Pharm. Chim.*, 1902, [6] 15, 97. Munson: U. S. Dept. Agr., Bur. Chem., Bull. 65, p. 53.

CHAPTER II.

Nitrogen, Sulphur and Phosphorus.

THE DETERMINATION OF NITROGEN.

The method of Dumas as outlined in the preceding chapter has the advantage of being applicable to all classes of nitrogen compounds. In the great majority of cases, however, it is equally accurate and much more convenient to use one of the methods based upon the conversion of nitrogen to ammonia and the determination of the latter by titration.

Before the introduction of the Kjeldahl process, the soda-lime method of Will and Varrentrap was commonly used. In this method the finely ground substance is mixed with a large excess of soda-lime and heated in a combustion tube, the ammonia given off being absorbed in standard acid. In order to ensure the reduction of nitro-compounds or nitrates, this method was modified by the introduction of stannous sulphide (Goldberg); of sodium formate and sodium thiosulphate (Arnold); or of sodium thiosulphate and a mixture of equal parts sulphur and powdered sugar or charcoal (Ruffle). The soda-lime method has now been very generally superseded by the various modifications of the Kjeldahl process.

The Kjeldahl Method.

In this process the substance is decomposed by heating with strong sulphuric acid, usually with the addition of some reagent which assists the decomposition either by raising the boiling point or by acting as a carrier of oxygen. When decomposition is complete the nitrogen remains as ammonium sulphate in the sulphuric acid, the carbon and hydrogen of the substance having been oxidized and the products of oxidation boiled out of the solution. The oxidation takes place partly at the expense of the sulphuric acid so that a considerable evolution of sulphur dioxide occurs, especially in the earlier stages of the process. After the completion of the digestion, the ammonia is liberated by means of fixed alkali and determined by distilling into standard acid. In the various modifications of the process, different reagents or combinations of reagents are used to hasten the decomposition of the organic matter by the sulphuric acid.

Kjeldahl originally directed *, that the substance be heated with sulphuric acid, with or without the addition of phosphoric anhydride, until a clear solution is obtained; then potassium permanganate added in small portions to the hot solution until it remains permanently colored, the permanganate being added very cautiously on account of the danger of a loss of nitrogen if the reaction becomes too vigorous.

Willfarth † introduced the use of mercuric oxide to facilitate the action of the sulphuric acid, and stated that if the solution be boiled until colorless neither phosphoric anhydride nor potassium permanganate need be used. In his earlier experiments Willfarth used copper instead of mercury. Arnold ‡ used both mercury and copper in addition to phosphoric anhydride.

Gunning § used for the digestion a simple mixture of sulphuric acid with one-third to one-half its weight of potassium sulphate. Arnold and Wedemeyer ‖ modified the Gunning process by the use of mercury and copper in addition to the potassium sulphate. By this modification the time required to decompose the organic matter was greatly reduced and good results were obtained with a number of alkaloids and other compounds which had not readily yielded the whole of their nitrogen when treated by the methods previously used. Independently Dyer ¶ obtained equally good results on a wide range of organic compounds by the use of mercury and potassium sulphate without copper.

The official agricultural chemists authorize ** the Kjeldahl-Willfarth and the Gunning methods for the analysis of foods, spices other than peppers, and fertilizers not containing nitrates. For peppers, to secure complete ammonification of the alkaloidal nitrogen, the Arnold-Wedemeyer modifidation of the Gunning method was provisonally adopted in 1902. In the experience of this laboratory, the Dyer modification has been found more rapid and slightly more accurate than either the Kjeldahl-Willfarth or Gunning method and fully as efficient in the case of alkaloids as is the Arnold-Wedemeyer method, while it has the advantage

* *Ztschr. anal. Chem.*, 1883, 22, 366.

† *Chem. Centrbl.* 1885 [3] 16, 17, 113.

‡ *Archiv. der Pharm.* [3], 24, 785; *Ztschr. anal. Chem.*, 1887, 26, 249.

§ *Ztschr. anal. Chem.*, 1889, 28, 188.

‖ *Ztschr. anal. Chem.*, 1892, 31, 525.

¶ *Journ. Chem. Soc.*, 1895, 67, 811.

** Bulletins 46 and 65, Bureau of Chemistry, U. S. Dept. Agriculture.

over the latter of requiring one less reagent and of yielding a colorless solution.

Applicability of the Kieldahl Method.—The Gunning-Arnold-Dyer modification, which for the reasons just mentioned is recommended for general use, is applicable to all classes of animal and vegetable substances, including such difficultly decomposable bases as betaine and the pyridine and chinoline alkaloids, and to cyanides, ferrocyanides and ferricyanides. It has also been tested * with good results on many other compounds, including acetanilid, sulphanilic acid, orthobenzoic sulphinid, amidobenzoic acid, benzamid, diamidophenol, naphthylamine, diphenylamine, diphenylthiourea, nitroso-dimethylaniline, indigotin, pyridine, and oxyphenyl methylpyrimidine.

Jodlbauer's modification,† devised for the determination of nitrogen in nitrates, was found by Dyer to be applicable to nitro-compounds, to azo-, hydrazo- and amidoazo-benzene, to carbazol and, with the addition of 1 or 2 grams of sugar, to hydroxylamine and oximes. Dyer did not obtain the whole of the nitrogen of hydrazine derivatives but Dafert‡ and Milbauer§ have published modifications which are said to give accurate results with this class of compounds.

Gunning-Arnold-Dyer Modification.

Reagents.— Pure concentrated sulphuric acid. Mercury. Pure potassium sulphate. Potassium sulphide solution, 40 grams per liter. Saturated solution of sodium hydroxide (commercial). Granulated zinc or pumice stone. Paraffin. Solution of methyl-orange, congo red, cochineal, lacmoid, or any other indicator suitable for titration in the presence of ammonium salts. Standard solutions of acid and alkali, preferably one-fifth or one-tenth normal.

Determination. — Weigh 0.5 to 5.0 grams sample, or so much as will probably yield from 50 to 75 milligrams of ammonia, and transfer to a pearshaped Kjeldahl flask of 550 to 750 c.c. capacity. Add 20 to 25 c.c. concentrated sulphuric acid and about 0.7 gram of mercury. Place the flask in an inclined position and heat gently until the first vigorous frothing ceases, then raise the heat grad-

* In some cases without the use of mercury. See in addition to the papers already cited, that of Gibson in the *Journal of the American Chemical Society*, 1904, 26, 105.

† *Chem. Centrbl.*, 1886, 3, 17, 433.

‡ *Landw. Versuchs-Sta.*, 1887, 34, 311.

§ *Ztschr. anal. Chem.*, 1903, 42, 725.

ually until the liquid boils; remove the flame for a few minutes, add 10 to 12 grams of potassium sulphate and boil. If the liquid is kept actually boiling, it will usually be clear and colorless within 30 minutes after the addition of the sulphate. Continue the boiling for at least 30 minutes after the solution becomes colorless or in any case for one hour from the time the potassium sulphate is added. If the sample contains alkaloids, the boiling should be continued for at least three hours in all and not less than two hours after the solution is colorless. When the digestion is finished, allow the flask to cool for 10 to 15 minutes or to 40°–60° (if allowed to become thoroughly cold the solution solidifies); then dilute carefully with 150 to 200 c.c. of water; allow to cool, add 25 c.c. potassium sulphide solution, mix well and then add 75 to 100 c.c. (or enough to make the reaction strongly alkaline*) of a cold saturated solution of sodium hydroxide, pouring it carefully down the side of the flask, so that it does not mix immediately with the acid solution. Add a few pieces of granulated zinc or pumice stone to prevent bumping, and a piece of paraffin the size of a pea to diminish frothing; connect the flask (preferably by means of a Hopkins' distilling head) with a condenser, the delivery tube of which dips into 50 c.c. of N/10 sulphuric or hydrochloric acid or its equivalent in the receiver; mix the contents of the flask by shaking and distil until about one-half of the liquid has passed into the receiver. Titrate the excess of acid in the receiver by means of standard alkali, using one of the indicators mentioned above.

The reagents used should be tested by making a blank determination with pure sugar or cellulose, carrying out all operations in exactly the same way as in a regular analysis.

Notes. — If in transferring the substance to the flask any particles or drops should lodge in the neck, they can be washed down by the sulphuric acid subsequently added. Dry samples can usually be weighed on a watchglass and brushed into the flask through a funnel having a wide stem which has been cut down to a length of about one cm., or transferred by means of a narrow strip of glazed paper. It is often more convenient to weigh the sample on, or transfer to, a small piece of pure filter paper, fold the latter loosely over the weighed portion and introduce the whole into the flask in such a way that the sample can be easily shaken

* Corallin (rosolic acid) may be used as indicator to show that the contents of the flask are alkaline before beginning the distillation.

free from the paper. The amount of cellulose thus introduced with the sample does not materially prolong the time required for digestion, while its reducing effect may aid in the ammonification of any firmly bound nitrogen present. Time should be allowed for thorough wetting of the sample by the sulphuric acid before heat is applied. During digestion a small funnel or balloon stopper may be placed loosely in the mouth of the flask to retard the evaporation of acid and guard against mechanical loss. The flask may rest upon a wire gauze, an iron plate or a piece of asbestos having a circular hole about 4 cm. in diameter which permits the free flame of the Bunsen burner to play upon the flask below the surface of the boiling liquid. The digestion should be conducted in a well ventilated hood where the air is free from any considerable amount of ammonia. In order to hasten the decomposition of organic matter, Dakin * and Milbauer (*l. c.*) recommend the use of potassium persulphate, while Krüger † suggests the addition of potassium dichromate in excess of the amount necessary to oxidize all carbon and hydrogen present. The method here described is, however, sufficiently rapid and more convenient for ordinary work.

The precipitation of mercury as sulphide before rendering the solution alkaline is to prevent the formation of mercur-ammonium compounds which do not readily yield their ammonia on boiling with caustic alkali. An ordinary Liebig condenser can be used in this distillation, though block tin tubing is generally preferred as being more resistant to the action of steam and ammonia. Unless the condenser tube is straight and nearly vertical, it is safer to rinse it out with a little cold distilled water at the end of the distillation and add the rinsings to the distillate. The distillation as usually carried out requires from forty minutes to one hour. Only about one third of this time is actually required to expel the ammonia from the boiling solution and if it is desired to hasten the operation, the steam can be conducted through tin tubing without condensation into a cooled receiver; or, as suggested by Benedict,‡ the water which cools the condenser may be drawn off after the solution has been boiling 15 minutes, and the boiling continued until enough steam has passed through to carry all of the ammonia from the condenser tube into the receiver. Fixed alkali is prefer-

* *Journ. Soc. Chem. Ind.*, 1902, 21, 848.

† *Ber. deut. chem. Ges.*, 1894, 27, 609.

‡ *Journ. Amer. Chem. Soc.*, 1900, 22, 259.

able to ammonia for the final titration since the latter reagent is liable to lose strength during use, probably through evaporation of ammonia from the tip of the burette and from the falling drop.

The reasons for preferring the method as above described to the original Kjeldahl-Willfarth or Gunning method have been briefly outlined above. If either of the latter methods is used, the same details of manipulation may be followed except that the digestion should be continued for at least two hours after the solution becomes colorless and not less than three hours in all. Even with this longer time of boiling the results are often slightly low. For the results of a comparative study of the Kjeldahl-Willfarth, the Gunning, and the above described method with special reference to the time of boiling required see the *Journal of the American Chemical Society* for April and November, 1904.

Method for Nitrates and Nitro-compounds.

The loss of nitric acid which might otherwise occur when sulphuric acid is poured upon a sample containing nitrates, is avoided by having present some substance which is very easily nitrated. such as salicylic acid, benzoic acid or phenol. The nitrogen having been thus fixed as a nitro-compound, the latter may be reduced by the addition of zinc dust (Jodlbauer) or sodium thiosulphate (Forster) after which the determination is carried out in the usual manner.

Reagents. — Sulphuric-salicylic acid, prepared in advance by dissolving salicylic acid in pure concentrated sulphuric in the proportion of 2 grams of the former to 30 c.c. of the latter. Zinc dust, an impalpable powder; or crystallized sodium thiosulphate. Other reagents as for the method above described.

Determination.— To the weighed portion of substance in a Kjeldahl flask, add 30 c.c. of the sulphuric-salicylic acid solution and shake until thoroughly mixed; then add 5 grams crystallized sodium thiosulphate, or add gradually with constant shaking 2 grams of zinc dust; warm gently until frothing subsides and then boil until thick white fumes cease to be given off. Allow to cool somewhat, add mercury and potassium sulphate and complete the process as described above. Or the potassium sulphate may be omitted and the oxidation completed by means of permanganate as in the 'modified Kjeldahl' method of the official agricultural chemists.

Notes.— Thiosulphate is the more convenient reducing agent

and can be safely used if the amount of nitric nitrogen is small. Zinc dust appears to be a safer reagent for samples rich in nitrates. In the presence of considerable amounts of chloride or of ammomium salts there is danger of a loss of nitrogen as oxide when the sample is treated with the sulphuric-salicylic acid mixture. In such cases the latter mixture should be thoroughly cooled before using and then poured as quickly as possible over the sample and the flask allowed to stand with occasional shaking for at least half an hour before the reducing agent is added. Ten minutes should be allowed for the reduction to take place before the solution is heated. With these precautions the loss of nitrogen will be reduced to an amount too small to be appreciable in ordinary work.

THE DETERMINATION OF SULPHUR.

In the various methods employed for the determination of sulphur, organic matter is destroyed by oxidation and the resulting sulphuric acid is precipitated and weighed as barium sulphate in the usual way. The chief difficulty lies in securing complete oxidation without loss, since many substances contain sulphur in forms from which it is easily liberated as volatile compound.

Comparative Outline of Methods.

The principal methods of bringing about the oxidation of the organic matter are:

1. By heating with nitric acid or an oxidizing acid mixture.
2. By burning in a combustion tube in a current of air, oxygen or some oxidizing vapor.
3. By heating in the presence of alkali and completing the reaction by the addition of an oxidizing agent.
4. By combustion in oxygen in a closed vessel.

Since the choice of a method depends on the nature of the sample to be examined and the apparatus at hand, no fixed rules can be laid down for this purpose. Several of the more important methods are therefore outlined and three methods which are especially useful for plant and animal substances are given in full.

Of methods of the first group, that of Carius, which has already been mentioned in the previous chapter, is the most important. It is applicable to volatile as well as to non-volatile substances, but is somewhat troublesome and tedious, and determinations are frequently lost through breaking of the heated tubes, especially when

much gas is produced by the oxidation of the carbon of the sample. For this reason only a small amount of any highly carbonaceous substance can be taken for analysis and often the amount of sulphuric acid obtained is too small for satisfactory determination.

Several methods belonging to the second group have been proposed. Among the more important are: (*a*) The method of Brugelmann,* in which the substance is burned in a current of oxygen, complete oxidation being insured by passing the mixture of gases over hot platinum, and absorbing the sulphuric acid in a column of soda-lime. If the substance is poor in sulphur several portions can be burned before dissolving out the lime and determining the sulphuric acid. (*b*) Mixter's modification† of Sauer's method. This consists in burning the substance in a current of oxygen and passing the products of combustion into bromine water. (*c*) Cläsown's‡ method of burning in a current of nitric oxide. (*d*) Barlow's method § in which the substance is burned in a current of oxygen in a specially constructed tube and complete oxidation is insured by means of a second current of oxygen introduced laterally at a point between the boat and the absorbing column. Methods of this type, carefully carried out, ensure complete oxidation and several portions of a sample may be burned in succession so as to secure a larger amount of sulphuric acid for determination. They are, however, less rapid than the methods described below, which are usually quite as accurate.

Liebig destroyed organic matter and converted sulphur to sulphate by heating with a mixture of caustic alkali and alkaline nitrate and methods of this type have been very generally used for plant and animal materials and other non-volatile substances. Of the many modifications of Liebig's method, the use of sodium peroxide as an oxidizing agent is most important. The peroxide may be used in connection with hydroxide as in Osborne's method, or the sample may be mixed at once with an excess of peroxide and ignited in a closed crucible || or in the combustion chamber of the Parr calorimeter.¶

* *Ztschr. anal. Chem.*, 1876, 15, 1, 175; 1877, 16, 1.

† *Amer. Chem. Journ.*, 1880, 2, 396.

‡ *Ber. deut. chem. Ges.*, 1886, 19, 1910; 1887, 20, 3065.

§ *Journ. Amer. Chem. Soc.*, 1904, 26, 341.

|| Sundstrom: *Journ. Amer. Chem. Soc.*, 1903, 25, 184. Pennock and Morton: *Ibid.*, 25, 1265.

¶ Parr: *Journ. Amer. Chem. Soc.*, 1900, 22, 646; 1904, 26, 1139. Konek: *Ztschr. angew. Chem.*, 1903, 516. Leclerc and Dubois: *Journ. Amer. Chem. Soc.*, 1904, 26, 1108.

Berthelot, in proposing the use of the oxygen calorimeter for the elementary analysis of organic materials, * stated that on combustion with 25 atmospheres of oxygen the sulphur was completely oxidized and in the presence of moisture could be quantitatively recovered as sulphuric acid. This method has been found both convenient and accurate. Complete oxidation takes place instantaneously, and since the combustion chamber is hermetically sealed there is no possibility of a loss of volatile compounds. As noted in the preceding chapter, a small autoclave may be used for the combustion if a bomb calorimeter is not available. According to Hempel † the sample can be burned in a large glass bottle filled with oxygen at atmospheric pressure.

The nature and number of the samples to be analyzed will usually determine which of the above methods is to be preferred. For the majority of cases either Liebig's or Osborne's method, or if the facilities are available, Berthelot's method of combustion in compressed oxygen may be recommended.

Liebig's Alkali Method.

In a large silver or nickel crucible mix about 8 grams potassium hydroxide and about 1 gram potassium nitrate. Fuse and stir with a silver or nickel spatula. Allow to cool and add 1 to 2 grams of the finely pulverized sample. Heat gently and as soon as the mass softens, stir well so as to bring the whole of the sample into contact with the alkali before it is strongly heated, then gradually increase the heat, stirring frequently to keep down frothing, and continue heating until the mass becomes colorless. For samples which react violently when stirred into the alkali as above, a smaller proportion of nitrate should be used at the beginning, or the nitrate may be omitted at the start and added after the sample has been mixed with the fused hydroxide. If the substance is not quickly oxidized by the fusion mixture, small amounts of pulverized nitrate may be added from time to time and the heating continued with frequent stirring. The fusion will usually be perfectly colorless when the oxidation of organic matter is complete. After cooling dissolve the fusion in water, in a beaker or casserole, acidulate with hydrochloric acid and evaporate to dryness to expel nitric

* *Compt. Rend.*, 1892, 114, 318; 1899, 129, 1002. See also Hempel: *Ber. deut. chem. Ges.*, 1897, 30, 202, and Langbein: *Ztschr. angew. Chem.*, 1900, 1227, 1259.

† *Ztschr. angew. Chem.*, 1892, 393. See also Graeffe: *Ibid.*, 1904, 616.

and nitrous acids and heat at 110° to dehydrate silica if present. If much nitrate or silica was present the evaporation with hydrochloric acid should be repeated. Dissolve the residue in cold water, adding a few drops of hydrochloric acid, filter if not perfectly clear, heat the solution to boiling and precipitate at the boiling temperature by adding a solution of barium chloride, drop by drop with constant stirring, until in considerable excess. Boil 5 or 10 minutes longer and allow to stand in a hot place until the precipitate settles, leaving the supernatant liquid perfectly clear. Filter and wash the barium sulphate, first with water acidulated with hydrochloric acid, then with water till free from chlorides and finally ignite and weigh with the usual precautions.

Notes and Precautions. — The reagents should be tested by making a "blank" determination with sugar or cellulose. Do not reject this blank if no precipitate appears when the barium chloride is added, but allow the solution to stand over night, to ensure the separation of any small amount of barium sulphate present, then filter, wash, ignite and weigh, and subtract the weight from that of the precipitate found in the determination. An apparently trifling amount of precipitate in the "blank" may weigh enough to appreciably affect the results. If the fusion is heated by an ordinary gas flame it is likely to absorb sulphur compounds from the latter. To avoid this use an alcohol flame for heating the fusions. It cannot be expected that the blank determination should show accurately the sulphur absorbed from the gas flame. Even when an alcohol flame is used and the sulphur obtained from the reagents is deducted, the results are sometimes too high. According to Keiser * this is chiefly due to the fact that the fused alkali takes up some silver from the crucible and, on acidifying with hydrochloric acid, the silver chloride formed is held in solution by the excess of potassium chloride present and is afterward carried down by the barium sulphate, increasing the weight of the precipitate. Keiser therefore recommends that the neutralized solution be cooled, diluted with water to about a liter and allowed to stand. Any silver chloride present will then precipitate and may be filtered out before adding barium chloride.

A modification which is often useful consists in heating the substance with strong nitric acid until a considerable part of the organic matter has been oxidized, after which an excess of alkali is

* *Amer. Chem. Journ.*, 1883, 5, 207.

added and the mixture transferred to a crucible and carefully fused until oxidation is complete. Hammarsten* found this method to give the same results as the methods of Liebig and of Clässon when applied to casein, egg albumen and gelatin.

Osborne's Peroxide Method.†

Convert about 10 grams of sodium peroxide into hydroxide by adding to it, in a silver or nickel crucible, a slight excess of water and heating until the excess is boiled off. Allow the fusion to cool until pasty, then add one to two grams of the sample and stir it into the alkali as quickly as possible. Heat gently and stir well to keep down the frothing. When the first vigorous action is over, heat until the mass fuses and stir in small portions of fresh peroxide until decomposition is complete and the fusion is practically colorless. Then allow to cool, dissolve the fusion and acidulate with hydrochloric acid; boil to destroy any excess of peroxide and to expel chlorine and complete the determination as in Liebig's method.

Notes. — Blank determinations must be made as in the case of the Liebig method, and the same precautions observed to prevent the absorption of sulphur compounds from gas flames or from the air of the laboratory. There is also the same danger of high results from contamination of the barium sulphate precipitate. If silica is absent the acidulated solution need not be evaporated to dryness since no nitrate is used in the fusion. For all such cases the method is considerably more rapid than that of Liebig, though requiring somewhat more careful attention during the fusion of the substance with the alkaline oxidizing mixture. This method has been extensively used during recent years in the analysis of proteids, food materials and physiological products and has lately been adopted by the Association of Official Agriculture Chemists. Several methods involving the use of sodium peroxide had previously been proposed, of which that of Asboth* is perhaps the best known. This consists in mixing the substance with 10 grams of dry sodium carbonate and 5 grams of peroxide in a nickel crucible and heating carefully at first and then more strongly until oxidation is complete. After dissolving the fusion in water the

* *Ztschr. physiol. Chem.*, 1885, 9, 273.

† *Journ. Amer. Chem. Soc.*, 1902, 24, 142.

* *Chem. Ztg.*, 1895, 19, 2040.

solution may be boiled with bromine to ensure complete oxidation. The alkaline mixture here used being much less fusible than sodium or potassium hydroxide, the method should be used only for such substances as do not readily lose sulphur on heating. For such substances it offers the advantage of simplicity in manipulation.

Berthelot's Oxygen Method.

Press into the form of a pellet a suitable amount of the substance (usually one to three grams), introduce into the bomb calorimeter and burn in oxygen under a pressure of about 25 atmospheres in the same manner as in the determination of heat of combustion.* Screw into the exit tube of the bomb a coupling carrying a delivery tube of about 0.5 mm. internal diameter and connect with a washing cylinder containing a little water. Carefully open the valve and allow the gas to bubble through the water until the contents of the bomb reach atmospheric pressure; then disconnect, open the bomb and rinse out all moisture which has condensed in the chamber, on the lining of the cover, or on the rods which support the combustion capsule. This must be done carefully as the rinsings usually contain the greater part of the sulphur. In order to keep down the volume of the solution, the water from the washing cylinder may be used for the first rinsing. Dissolve any ash found in the combustion capsule in a little hydrochloric acid, remove silica, if necessary, and add the solution to that obtained by rinsing the bomb. Examine the lead gasket in the cover of the bomb and if a slight film of sulphate is found, wash it into the main solution.† Finally boil this solution down to the desired volume, neutralize any excessive amount of hydrochloric acid which may have been introduced with the solution of the ash, filter if necessary and determine the sulphuric acid by precipitation with barium chloride as already described.

Notes. — This method, based mainly upon the suggestion of Berthelot and the subsequent work of Hempel, has been applied‡ with very satisfactory results to a number of animal and vegetable substances as well as to synthetic organic compounds containing sul-

* Atwater and Snell: *Jour. Amer. Chem. Soc.*, 1903, 25, 659.

† Such minute quantities of lead sulphate as are ordinarily found will dissolve readily in the solution and will not interfere with the precipitation of sulphuric acid as barium sulphate.

‡ *Jour. Amer. Chem. Soc.*, 1902, 24, 1100.

phur in forms not readily oxidized to sulphuric acid — *e. g.*, benzyl sulphide and diphenyl-thiourea. So far as tested, no cases of incomplete combustion have been found. If this were suspected, the gas drawn off after the combustion should be led through bromine water or an alkaline bromine solution and the washings of the bomb added to this solution and boiled to insure oxidation of sulphites to sulphates. Unless the bomb is emptied gradually in some such way as has been described, there is danger that some sulphuric acid may be carried away mechanically by the escaping gas. This is probably the principal cause of the low results occasionally reported. When properly carried out this method has several important advantages. Combustion takes place instantaneously and with no chance for the escape of volatile products. The products of combustion can be drawn off and examined as desired. The only reagents required in obtaining the sulphur as sulphuric acid are compressed oxygen and hydrochloric acid, both of which are easily obtained free from any appreciable amounts of sulphur. By eliminating the use of alkali, any danger of absorption of sulphur compounds from the air is avoided, and no considerable amount of foreign salts is introduced into the solution from which the sulphuric acid is to be precipitated.

THE DETERMINATION OF PHOSPHORUS.

The oxidation of organic matter for the determination of phosphorus may be accomplished by any of the methods described in connection with the sulphur determination. It is of course unnecessary in this case to avoid the use of gas flames and with most substances there is much less danger of loss by volatilization than in the case of sulphur. For these reasons and because of the care required in dissolving the fused residue of phosphates left in the ignition capsule, the compressed oxygen method has no such marked advantages in the determination of phosphorus as in that of sulphur.

Alkali Methods.

Liebig's method of oxidation, either with or without previous digestion with nitric acid, or oxidation by peroxide may be used but the use of sodium carbonate, as in the following method, is generally more convenient.

Mix 1 to 3 grams substance with 6 to 7 grams dry sodium carbonate in a platinum dish and spread 3 or 4 grams of the carbonate

over the mixture. Heat over a Bunsen burner, carefully at first until frothing ceases, then strongly until the mass fuses. To the fusion add small portions of pulverized potassium nitrate, stirring thoroughly with a platinum rod or spatula, until the mass is entirely colorless. The whole amount of nitrate required usually does not exceed one gram. After cooling, transfer the fusion to a beaker, dissolve in water, add an excess of nitric acid and boil. Allow the solution to cool, neutralize with ammonia, add a few drops of nitric acid and then a moderate excess of molybdate solution.* Digest at about 65° for an hour with occasional shaking or stirring, filter, and wash with cold water or a cold solution of ammonium nitrate. Test the filtrate by adding more molybdate solution and digesting again at about 65°. Place the beaker used for the precipitation under the funnel, dissolve the precipitate through the paper by means of ammonia and wash thoroughly with water, keeping the volume of the solution below 100 c.c. Nearly neutralize with hydrochloric acid, cool thoroughly and add a moderate excess of magnesia mixture,† drop by drop, with constant stirring. After 15 minutes add 10 c.c. of concentrated ammonia or its equivalent; let stand four to twenty-four hours; filter (preferably on an asbestos felt in a Gooch crucible) wash with dilute ammonia (2.5 to 5 per cent.) until practically free from chlorides, ignite and weigh as magnesium pyrophosphate.

Neumann's Acid Method.‡

To 1 to 3 grams substance in a Kjeldahl flask add 20 c.c. concentrated sulphuric acid and 10 grams of ammonium nitrate and heat carefully until frothing ceases; or heat the sample first with 10 c.c. fuming nitric acid, then cool and add 10 c.c. of sulphuric acid. In either case the solution is boiled with successive additions of ammonium nitrate until organic matter is entirely destroyed and the solution is colorless. If necessary, as many grams of ammonium nitrate may be added as the number of c.c. of sulphuric acid used. Cool the colorless solution, wash it out into a

* Of the usual molybdate solution containing about 5 per cent. of molybdic acid, add at least 50 c.c. for every decigram of phosphoric acid expected.

† If the magnesia mixture is of the usual strength, containing about 5 per cent. of magnesium chloride, add about 15 c.c. for each decigram of phosphoric acid expected.

‡ *DuBois Reymond's Archiv.* (physiol. Abth.), 1897, 552; 1900, 159; Abs. *Chem. Centrbl.*, 1900, I., 571. See also *Ztschr. physiol. Chem.*, 1900, 29, 146; 1902-3, 37, 115; *Journ. Amer. Chem. Soc.*, 1902, 24, 1100.

beaker, neutralize with ammonia, add 15 to 20 grams of ammonium nitrate and determine phosphoric acid as in the preceding method, adding a somewhat greater excess of the molybdate reagent.

Notes. — This method has been found to give good results with a variety of foods and physiological products. The large amount of sulphates retards the formation of the phosphomolybdate precipitate, but by using liberal quantities of ammonium nitrate and molybdate reagent and allowing at least an hour for the precipitation, the whole of the phosphoric acid is obtained without difficulty. When the substance is first treated with fuming nitric acid, a smaller quantity of sulphuric acid may be used and the phosphomolybdate will then form somewhat more quickly.

In applying this method to liquids such as milk or urine, a suitable amount of sample (25 c.c. milk or 50 c.c. urine,) is transferred to the flask, 20 c.c. sulphuric acid added, and the mixture heated carefully as in the determination of nitrogen until the sample is well charred and the greater part of the water has been boiled off. Ammonium nitrate is then added and the determination is completed as above described.

For additional notes on this method and a discussion of methods for the separation of organic and inorganic phosphorus in plant, and animal products, see Hart and Andrews, *Amer. Chem. Journ.* 1903, 30, 470.

CHAPTER III.

Alcohols.

Alcohols being usually defined as neutral hydroxyl derivatives capable of reacting with acids to form esters, it follows that the most characteristic alcohol reactions are those involving the replacement of the hydroxyl by an acid radical. For detailed discussions of the analytical behavior of the hydroxyl radical and characteristic reactions of the different groups of alcohols, the reader is referred to the works of Hans Meyer,* while Mulliken's tables † may be followed in the systematic identification of individual pure preparations.

Of the analytical methods involving reactions of the hydroxyl group, the more important are those in which the acetyl or benzoyl ester is formed. The preparation of the dinitrobenzoate serves for the identification of ethyl alcohol as described below. Quantitative methods based on acetylation will be described in the sections on glycerol and the fatty oils. Often, however, esterification is either not quantitative or is less convenient or less delicate than other methods of determination. Thus all monatomic alcohols containing less than four carbon atoms mix freely with water and are not readily separated from it but may be determined in aqueous solution either by physical methods or by the behavior of the acohols on oxidation.

The present chapter will be devoted essentially to ethyl alcohol and glycerol. The processes described for the quantitative determination of these compounds include the application of physical methods, methods of oxidation and methods of acetylation. In connection with the determination of ethyl alcohol, special methods for the detection or determination of a few of its more important homologues will be briefly outlined. For more extended discussions of the analytical chemistry of the alcohols the work of Allen ‡ should be consulted.

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* Analyse und Konstitutionsermittelung organischer Verbindungen, Berlin, 1903. Determination of Radicles in Carbon Compounds (English Edition by Tingle), New York, 1903.

† Identification of Pure Organic Compounds, New York, 1904.

‡ Commercial Organic Analysis, Volume I, Philadelphia, 1898.

ETHYL ALCOHOL.

Pure ethyl alcohol is a colorless, mobile liquid of characteristic penetrating odor and "hot" pungent taste, boiling at about 78.4°. It mixes with water in all proportions and is only with great difficulty obtained in the anhydrous or "absolute" state. According to Allen the presence of as small a proportion as 0.5 per cent. of water in alcohol is indicated by the pink color assumed by the liquid on introducing a crystal of potassium permanganate. The so-called "absolute alcohol" used in analytical operations ordinarily contains from 0.2 to 1 per cent of water.

Until recently the density of anhydrous alcohol at 60° F. (15.55° C.) was considered to be 0.79381 referred to water at the same temperature. Squibb obtained alcohol which, while not absolutely anhydrous, had a density of only 0.79350 at 60° F. indicating that the alcohol previously considered absolute must have contained at least 0.1 per cent. of water.

On mixing alcohol with water a considerable evolution of heat takes place and the volume of the mixture after cooling is less than the sum of the volumes of alcohol and water mixed. This contraction is not uniformly proportional to the amount of alcohol in the mixture. Hence in mixtures of water and alcohol the relation between the percentages of alcohol "by volume" and "by weight" varies somewhat with the strength of the solutions. These variations together with the differences in the density of the supposedly absolute alcohol used as standard by the various observers, account for the small discrepancies found on comparing the commonly used tables showing the relation between density and percentage. Thus the table of Windisch which is usually given in German textbooks, that of Allen which appears to be based on Hehner's table, and that of Edgar Richards based mainly on the work of Squibb, is each different, though the variations are rarely sufficient to be noticeable in ordinary work.

Alcohol dissolves many organic substances which are not soluble in water, but inorganic compounds insoluble in water are usually also insoluble in alcohol. As a rule chlorides, bromides, iodides, and acetates are soluble in fairly strong alcohol, while carbonates, borates, sulphates, phosphates, oxalates and tartrates are only very sparingly soluble.

Detection and Identification.

Lieben's Iodoform Test.

The "iodoform test" while not distinctive is often useful. It may be carried out as follows: To 10 c.c. of the clear liquid to be tested, add 5 or 6 drops of 10 per cent. solution of sodium or potassium hydroxide, heat to about 50° C. and add drop by drop with constant shaking a saturated solution of iodine in aqueous potassium iodide until the liquid becomes just permanently yellowish-brown, then carefully decolorize by adding more of the hydroxide solution, avoiding excess. If alcohol were present, iodoform gradually separates out as a yellow or yellowish-white crystalline deposit. Even when very little iodoform is produced its odor can usually be recognized. While the test is quite delicate, the appearance of a precipitate of iodoform does not prove the presence of ethyl alcohol since it may result from various other compounds, especially acetone, aldehydes and the propyl and butyl alcohols. If the original liquid contained carbohydrate or organic acid it should be neutralized, distilled and the first portion of the distillate used for the test.

Ethyl Dinitrobenzoate Test.

As a specific test for ethyl alcohol Mulliken * recommends the preparation of Ethyl 3, 5-Dinitrobenzoate as follows:

Heat together gently in a three-inch test-tube held over a small flame, 0.15 gm. of 3, 5-dinitrobenzoic acid and 0.20 gm. of phosphorus pentachloride. When signs of chemical action are seen, remove the heat for a few seconds. Then heat again, boiling the liquefied mixture *very gently* for one minute. Pour out on a very small watchglass and allow to solidify. As soon as solidification occurs, remove the liquid phosphorus oxychloride, with which the crystalline mass is impregnated, by rubbing the latter between two small pieces of porous tile. Place the powder in a dry five or six-inch test-tube. Allow four drops of the alcohol (which must contain not more than about 10 per cent. of water) to fall upon it, and then stopper the tube tightly without delay. Immerse the lower part of the test-tube in water having a temperature of 75°–85°. Shake gently, and continue the heating for ten minutes.

To purify the ester produced in the reaction, crush with a stirring rod, any hard lumps which may form when the mixture cools

* *Loc. cit.*, p. 168.

and boil gently with 15 c.c. of methyl alcohol (2 : 1) until all is dissolved or for a minute or two. Filter boiling hot if the solution is not clear. Cool, shake and filter. Wash with 3 c.c. cold methyl alcohol (2 : 1). Recrystallize from 9 c.c. of boiling methyl alcohol (2 : 1). Wash with 2 c.c. of the same solvent. Spread out the product on a piece of tile. Allow to become air-dry, and determine the melting point.

Ethyl 3, 5-Dinitrobenzoate, the product of this test crystallizes in white needles melting at 92°–93° (uncorr.).

The corresponding derivatives of methyl, propyl, butyl, and isobutyl alcohols melt at 107.5° (uncorr.), 73°–73.5° (uncorr.), 64° (uncorr.) and 83°–83.5° (uncorr.) respectively.

Determination by the Specific Gravity Method.

This method which is the most generally applicable and the most accurate for the determination of alcohol in ordinary alcoholic liquors, consists in obtaining the alcohol mixed only with water and determining the amount of alcohol present by finding the specific gravity of this aqueous solution. It will be convenient to describe first the method as applied to fermented liquors and then note the modifications to be introduced in the analysis of other alcohol preparations.

Alcohol in Fermented Liquors.

Dry and weigh a 100 c.c. graduated flask. Fill to the holding mark with the sample* and weigh. Transfer to a distilling flask of 250 to 300 c.c. capacity, rinsing out the measuring flask with about 50 c.c. of water. Add about one-tenth gram of calcium carbonate to neutralize any acid present, or carefully neutralize by means of dilute sodium or potassium hydroxide, connect with a well cooled condenser and distil, collecting the distillate in the flask used for measuring the sample. When the receiver is filled to the mark remove it, wipe the outside with a dry cloth and weigh. By means of a pyknometer determine accurately (to five decimal places) the specific gravity of the distillate at 15.55° C. (60° F.) compared with recently boiled distilled water at the same

* If the sample contains much carbon dioxide this should be removed as far as possible in advance by shaking the liquor in a large flask at room temperature.

PERCENTAGE OF ALCOHOL BY WEIGHT AND BY VOLUME.

[Recalculated from the determinations of Gilpin, Drinkwater and Squibb, by EDGAR RICHARDS.]

Specific Gravity at 15.5° C.	Per Cent. Alcohol by Volume.	Per Cent. Alcohol by Weight.	Specific Gravity at 15.5° C.	Per Cent. Alcohol by Volume.	Per Cent. Alcohol by Weight.	Specific Gravity at 15.5° C.	Per Cent. Alcohol by Volume.	Per Cent. Alcohol by Weight.
1.00000	0.00	0.00	0.99281	5.00	4.00	0.98660	10.00	8.04
0.99984	.10	.08	268	.10	.08	649	.10	.12
968	.20	.16	255	.20	.16	637	.20	.20
953	.30	.24	241	.30	.24	626	.30	.29
937	.40	.32	228	.40	.32	614	.40	.37
.99923	0.50	0.40	.99215	5.50	4.40	.98603	10.50	8.45
907	.60	.48	202	.60	.48	592	.60	.53
892	.70	.56	189	.70	.56	580	.70	.61
877	.80	.64	175	.80	.64	569	.80	.70
861	.90	.71	162	.90	.72	557	.90	.78
.99849	1.00	0.79	.99149	6.00	4.80	.98546	11.00	8.86
834	.10	.87	136	.10	.88	535	.10	.94
819	.20	.95	123	.20	.96	524	.20	9.02
805	.30	1.03	111	.30	5.05	513	.30	.11
790	.40	.11	098	.40	.13	502	.40	.19
.99775	1.50	1.19	.99085	6.50	5.21	.98491	11.50	9.27
760	.60	.27	072	.60	.29	479	.60	.35
745	.70	.35	059	.70	.37	468	.70	.43
731	.80	.43	047	.80	.45	457	.80	.51
716	.90	.51	034	.90	.53	446	.90	.59
.99701	2.00	1.59	.99021	7.00	5.61	.98435	12.00	9.67
687	.10	.67	009	.10	.69	424	.10	.75
672	.20	.75	.98996	.20	.77	413	.20	.83
658	.30	.83	984	.30	.86	402	.30	.92
643	.40	.91	971	.40	.94	391	.40	10.00
0.99629	2.50	1.99	.98959	7.50	6.02	.98381	12.50	10.08
615	.60	2.07	947	.60	.10	370	.60	.16
600	.70	.15	934	.70	.18	359	.70	.24
586	.80	.23	922	.80	.26	348	.80	.33
571	.90	.31	909	.90	.34	337	.90	.41
.99557	3.00	2.39	.98897	8.00	6.42	.98326	13.00	10.49
543	.10	.47	885	.10	.50	315	.10	.57
529	.20	.55	873	.20	.58	305	.20	.65
515	.30	.64	861	.30	.67	294	.30	.74
501	.40	.72	849	.40	.75	283	.40	.82
.99487	3.50	2.80	.98837	8.50	6.83	.98273	13.50	10.90
473	.60	.88	825	.60	.91	262	.60	.98
459	.70	.96	813	.70	.99	251	.70	11.06
445	.80	3.04	801	.80	7.07	240	.80	.15
431	.90	.12	789	.90	.15	230	.90	.23
.99417	4.00	3.20	.98777	9.00	7.23	.98219	14.00	11.31
403	.10	.28	765	.10	.31	209	.10	.39
390	.20	.36	754	.20	.39	198	.20	.47
376	.30	.44	742	.30	.48	188	.30	.56
363	.40	.52	730	.40	.56	177	.40	.64
.99349	4.50	3.60	.98719	9.50	7.64	.98167	14.50	11.72
335	.60	.68	707	.60	.72	156	.60	.80
322	.70	.76	695	.70	.80	146	.70	.88
308	.80	.84	683	.80	.88	135	.80	.97
295	.90	.92	672	.90	.96	125	.90	12.05

PERCENTAGE OF ALCOHOL BY WEIGHT AND BY VOLUME.—*Continued.*

[Recalculated from the determinations of Gilpin, Drinkwater and Squibb, by EDGAR RICHARDS.]

Specific Gravity at 60° F.	Per Cent. Alcohol by Volume.	Per Cent. Alcohol by Weight.	Specific Gravity at 60° F.	Per Cent. Alcohol by Volume.	Per Cent. Alcohol by Weight.	Specific Gravity at 60° F.	Per Cent. Alcohol by Volume.	Per Cent. Alcohol by Weight.
0.98114	15.00	12.13	0.97608	20.00	16.26	0.97097	25.00	20.43
104	.10	.21	598	.10	.34	086	.10	.51
093	.20	.29	588	.20	.42	076	.20	.60
083	.30	.38	578	.30	.51	065	.30	.68
073	.40	.46	568	.40	.59	055	.40	.77
.98063	15.50	12.54	.97558	20.50	16.67	.97044	25.50	20.85
052	.60	.62	547	.60	.75	033	.60	.93
042	.70	.70	537	.70	.84	023	.70	21.02
032	.80	.79	527	.80	.92	012	.80	.10
021	.90	.87	517	.90	17.01	001	.90	.19
.98011	16.00	12.95	.97507	21.00	17.09	.96991	26.00	21.27
001	.10	13.03	497	.10	.17	980	.10	.35
.97991	.20	.12	487	.20	.26	969	.20	.44
980	.30	.20	477	.30	.34	959	.30	.52
970	.40	.29	467	.40	.43	949	.40	.61
.97960	16.50	13.37	.97457	21.50	17.51	.96937	26.50	21.69
950	.60	.45	446	.60	.59	926	.60	.77
940	.70	.53	436	.70	.67	915	.70	.86
929	.80	.62	426	.80	.76	905	.80	.94
919	.90	.70	416	.90	.84	894	.90	22.03
.97909	17.00	13.78	.97406	22.00	17.92	.96883	27.00	22.11
899	.10	.86	396	.10	18.00	872	.10	.20
889	.20	.94	386	.20	.09	861	.20	.28
879	.30	14.03	375	.30	.17	850	.30	.37
869	.40	.11	365	.40	.26	839	.40	.45
.97859	17.50	14.19	.97355	22.50	18.34	.96828	27.50	22.54
848	.60	.27	345	.60	.42	816	.60	.62
838	.70	.35	335	.70	.51	805	.70	.71
828	.80	.44	324	.80	.59	794	.80	.79
818	.90	.52	314	.90	.68	783	.90	.88
.97808	18.00	14.60	.97304	23.00	18.76	.96772	28.00	22.96
798	.10	.68	294	.10	.84	761	.10	.04
788	.20	.77	283	.20	.92	749	.20	.13
778	.30	.85	273	.30	19.01	738	.30	.21
768	.40	.94	263	.40	.09	726	.40	.30
.97758	18.50	15.02	.97253	23.50	19.17	.96715	28.50	23.38
748	.60	.10	242	.60	.25	704	.60	.47
738	.70	.18	232	.70	.34	692	.70	.55
728	.80	.27	222	.80	.42	681	.80	.64
718	.90	.38	211	.90	.51	669	.90	.72
.97708	19.00	15.43	.97201	24.00	19.59	.96658	29.00	23.81
698	.10	.51	191	.10	.67	646	.10	.89
688	.20	.59	180	.20	.76	635	.20	.98
678	.30	.68	170	.30	.84	623	.30	24.06
668	.40	.76	159	.40	.93	611	.40	.15
.97658	19.50	15.84	.97149	24.50	20.01	.96600	29.50	24.23
648	.60	.93	139	.60	.09	587	.60	.32
638	.70	16.01	128	.70	.18	576	.70	.40
628	.80	.09	118	.80	.26	564	.80	.49
618	.90	.18	107	.90	.35	553	.90	.57

temperature. Find in the accompanying table * the percentages of alcohol by weight and by volume corresponding to this specific gravity.

The percentage by weight of alcohol in the distillate, multiplied by the weight of the latter shows the actual weight of alcohol distilled over and this divided by the weight of sample taken, gives the percentage by weight of alcohol in the liquor. The percentage by volume is of course the same for the original sample as for the distillate, if both are measured in the same flask at the same temperature.

Alcohol in Other Solutions.

Distilled Liquors. — Take a smaller amount of the sample so as to have not over 25 grams of alcohol present. There should be no acid present to require neutralization. Dilute the portion taken for analysis to 150 c.c. in the distilling flask, distil until 100 c.c. have passed over and complete the determination as described.

Cordials, bitters, etc., which are likely to contain high percentages of both alcohol and extractive matters, should be diluted if necessary and treated as described for fermented liquors.

Preparations containing chloroform, ether, or essential oils, may be treated as follows: † Dilute 25 c.c. of the sample with water to about 100 c.c. in a separatory funnel, add sodium chloride to saturation and then 50 to 80 c.c. of light petroleum distillate (boiling below 60°). Shake vigorously for 5 minutes, allow to stand for half an hour, draw off the lower layer into another separatory funnel wash again in the same way with a small amount of the petroleum ether and then draw off into a distillation flask. Unite the petroleum ether layers, wash with two successive portions each 25 c.c. of water saturated with salt, adding these washings to the main solution. Neutralize if necessary and distil in the usual way.

Notes on the Specific Gravity Method.

When the distillation is carried out as above described, 100 c.c. being distilled from an original volume of about 150 c.c. containing not more than 25 grams of alcohol, the distillation may be carried on at a fairly rapid rate. There is no danger that the whole of the alcohol will not be distilled over, and if the condenser is kept

* Condensed from the tables adopted by the Association of Official Agricultural Chemists, Bulletins 46 and 65, Bur. Chem., U. S. Dept. Agriculture.

† Thorpe and Holmes: *Journ. Chem. Soc.*, 1903, 83, 314.

cooled to room temperature and is properly connected with the receiver, only traces of alcohol need be lost by evaporation. The delivery tube of the condenser may either extend well into the neck of the receiving flask or may be connected with it by means of an "adapter." If unusual precautions to avoid evaporation are desired the receiver may be closed with a stopper having one hole to admit the adapter and another fitted with a small reflux condenser, which can be rinsed with a few drops of water toward the end of the operation.

It is necessary to exercise great care in the determination of the specific gravity of the distillate, especially as regards the temperature at which the pyknometer is filled. If this is different from the temperature for which the table is constructed, each weighing must be separately reduced to standard temperature since alcohol and water do not expand at the same rate. The safest way, both in calibrating the pyknometer and in making the determination, is to cool the liquid to a little below 15.5°, fill, and allow the temperature to rise slowly until the proper point is reached, then adjust the pyknometer, wipe it dry on the outside and weigh. Never hold the pyknometer, in such a manner that the temperature of its contents can be affected by the warmth of the hand. Find the weight of water which the pyknometer holds at 15.5°* and use this as divisor in estimating the specific gravity of the distillate. Empty and dry the pyknometer, fill with distillate at 15.5° and weigh. If both observations are made at 15.5°, the weight of distillate divided by that of water gives the desired specific gravity. If the pyknometer is filled with distillate at a few degrees above or below 15.5°, the weight must be divided by the weight of water at 15.5° to find the "apparent specific gravity", then correct this by the following empirical formula given by Allen† in which D is the specific gravity at 15.5°, D' the "apparent" specific gravity, and d the difference (in degrees centigrade) between 15.5° and the temperature at which D' was determined:

$$D = D' \pm d\left(0.00014 + \frac{1 - D'}{150}\right).$$

* If for any reason the water is slightly above or below 15.5°, note the temperature accurately, divide the weight of water found by the weight of 1 c.c. at that temperature and multiply by 0.999055. The following may be taken as the weight of 1 c.c. of water in grams at the temperatures given: 13°, 0.999410; 14°, 0.999278; 15°, 0.999134; 16°, 0.998976; 17°, 0.998808; 18°, 0.998629; 19°, 0.998438; 20°, 0.998235; 21°, 0.998023; 22°, 0.997801; 23°, 0.997568.

† Commercial Organic Analysis, Vol. I. (3d Ed.), p. 93.

The correction is added to, or subtracted from, the "apparent specific gravity" according as the pyknometer was filled at a temperature above or below the standard.

The specific gravity of the distillate being known to five decimal places, its alcohol content by weight and by volume can be found to the second decimal place by intercalculation between the values given in the table.

Pyknometers. — In using the ordinary form of specific gravity bottle having a simple ground glass stopper with capillary bore, care must be taken that no minute bubbles of air are entrapped when the stopper is inserted. This may be largely avoided by grinding the lower end of the stopper either convex or concave. When a pyknometer of this form is allowed to stand at a higher temperature than that at which it has been filled, the expansion forces some of the liquid out upon the top of the stopper, whence it may be lost either mechanically or by evaporation. Since the temperature of the laboratory is usually considerably above 15.5°, the weighing should be made as promptly as possible. The Geissler pyknometer has a thermometer inserted in the ground glass stopper so that the temperature of the contents can be read directly at any time. A side tubulure of small bore provides for the overflow at constant volume and is fitted with a ground glass cap, so that when the adjustment has been made there is no danger of a loss of contents in case the pyknometer is allowed to stand for a time at a higher temperature. Squibbs' pyknometer * has a body like an ordinary specific gravity bottle, but the ground neck is fitted with a narrow graduated stem instead of a stopper. Adjustment is secured by removing small portions of liquid from this stem by means of a capillary pipette and narrow strips of blotting board. The construction of the instrument makes it easy to observe when the contents are at the same temperature as the surrounding medium, since as long as any expansion or contraction is taking place, the column of liquid will move up or down in the stem. This instrument, like that of Geissler, avoids all inconvenience from overflow during weighing. It is especially useful when one wishes to use the same pyknometer for determinations of specific gravity at different temperatures. Ostwald objects to any pyknometer having a tight stopper on the ground that "as the conical angle of the stopper must be small in order to get it to

* *Journ. Amer. Chem. Soc.*, 1897, 19, 111.

fit tight, a slight elastic deformation of the neck causes a considerable displacement of the stopper in the direction of its axis," thus introducing a source of error not easily avoided. He therefore recommends* a modification of the Spengel pyknometer which has now come into quite common use. With care in avoiding the sources of error which have been mentioned, any standard form of pyknometer should give satisfactory results.

Determination by the Boiling Point Method.

In mixtures of alcohol and water containing no appreciable amount of other volatile substances and only small quantities of dissolved solids, the difference between the boiling point of the mixture and that of pure water under the same conditions, gives a measure of the percentage of alcohol present. For the rapid determination of alcohol on this principle, several forms of ebullioscope have been devised. The liquid to be tested is boiled under a reflux condenser while a thermometer bulb is fixed just above the surface of the liquid so as to be entirely surrounded by the vapor. The more common technical forms, such as those of Pohl and Kappeller, have scales reading percentage of alcohol instead of thermometer scales. Water is first boiled in the apparatus and the scale adjusted so that the mercury stands at zero. If then the water be removed and the sample introduced and brought to boiling under the same barometric conditions, the point reached by the mercury column shows the amount of alcohol present.

Wiley† uses a delicate differential thermometer with an apparatus similar to that employed for the determination of molecular weights by the boiling point method. Up to five per cent. of alcohol, the depression of the boiling point is said to be so regular that the results are entirely satisfactory for practical work. In the ebullioscopes bearing scales graduated in terms of alcohol, the variations in the boiling point curve at the higher percentages are, of course, allowed for. The boiling point method is very rapid and gives results sufficiently accurate for many purposes. Reference may be made to Vaubel‡ for a general discussion of methods based on the determination of the boiling point and to

* Ostwald: Physico-Chemical Measurements (translated by Walker), New York, 1894. The Sprengel-Ostwald pyknometer is also described by Getman: Laboratory Exercises in Physical Chemistry, New York, 1904.

† *Journ. Amer. Chem. Soc.*, 1896, 18, 1063.

‡ Quantitative Bestimmung organischer Verbindungen. Berlin, 1902.

Freyer* for experimental results on the influence of dissolved solids in the ebullioscopic determination of alcohol.

Determination by Oxidation.

Under suitable conditions ethyl alcohol can be quantitatively oxidized to acetic acid by means of potassium dichromate in the presence of sulphuric acid. The amount of alcohol can then be ascertained either by determining the amount of dichromate reduced† or by distilling and titrating the acetic acid formed.‡ The conditions of oxidation must be carefully regulated and as a rule the method is used only for the determination of very small amounts of alcohol, the specific gravity method being preferable for the examination of any but very dilute solutions. The alcohol must of course be separated by distillation from any other oxidizable matter before the oxidation method can be applied. A comparison of the results obtained by oxidation with those shown by the specific gravity method may be useful in demonstrating the presence of homologous alcohols.

Detection and Determination of Homologous Alcohols.

Methyl Alcohol.

In many countries "methylated spirit" (usually a mixture of 9 parts ethyl alcohol with 1 part commercial wood spirit) is exempt from the taxes levied upon other forms of alcohol. The former is therefore much cheaper and there is great inducement to substitute it for pure ethyl alcohol in the preparation of tinctures, etc., where its use is, however, highly objectionable on account of the toxicity of the methyl alcohol. Under such circumstances the detection of small amounts of methyl alcohol or wood spirit is often of importance. In the United States, "methylated spirit" is not exempt from taxation (1904) and delicate tests for its detection are therefore of much less practical importance. Methyl alcohol itself may be fraudulently substituted for ethyl alcohol but this would be profitable only when considerable quantities were involved and in such cases the presence of the methyl alcohol should be shown by quantitative methods.

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* *Ztschr. angew. Chem.*, 1896, 654.

† Hehner: *Analyst*, 1887, 12, 25. Benedict and Norris: *Journ. Amer. Chem. Soc.*, 1898, 20, 293.

‡ Dupre: *Journ. Chem. Soc.*, 1867, 20, 495.

Aqueous solutions of methyl alcohol have specific gravities so close to those of ethyl alcohol of the same strength that the total amount of the two alcohols can be determined by distilling, taking the specific gravity of the distillate and calculating the percentage from the ethyl alcohol table. This distillate may then be examined for methyl alcohol by one of the following methods.

Color Reactions.—The color reactions now commonly used * depend upon oxidation of the methyl alcohol to formaldehyde which is then detected by one of the tests described in the next chapter. These tests can be depended upon only when very carefully carried out with attention to the precautions given by Mulliken and Scudder, † while great care must also be exercised in the interpretation of the tests inasmuch as positive reactions for methyl alcohol have been obtained ‡ in the case of a number of genuine wines and brandies.

The Iodide Method of Lam § is based upon the fact that methyl iodide is considerably heavier than ethyl iodide, the former having at 15° a specific gravity of 2.2677, while that of the latter is 1.9444. The mixture of alcohols to be tested is treated with red phosphorus and iodine and the resulting iodides distilled, purified, dried and weighed. A determination of specific gravity shows the percentage of methyl iodide in the mixture and from this the percentage of methyl alcohol in the original sample. Ethyl alcohol is not completely transformed into iodide, but according to Lam the transformation of the methyl alcohol is quantitative.

The Oxidation Method of Thorpe and Holmes ‖ is simpler and more direct. It depends upon the oxidation of the mixture of ethyl and methyl alcohols under such conditions that the former is converted into acetic acid while the latter is completely oxidized to carbon dioxide and water. The total amount of alcohols having been determined as above, a part of the distillate is mixed with water in such proportions that 50 c.c. of the mixture shall contain not more than 1 gram of methyl alcohol nor more than 4 grams of ethyl and methyl alcohols together. Fifty c.c. of this mixture are introduced

* Mulliken and Scudder: *Amer. Chem. Journ.*, 1900, 24, 444. Prescott: *Pharmaceutical Archives*, 1901, 4, 86. Bulletin 65, Bur. Chem., U. S. Dept. Agriculture.

† *Loc. cit.*

‡ Trillat: *Compt. rend.*, 1899, 1. Wolff: *Ztschr. Unters. Nahr.-Genussm.*, 1901, 4, 391.

§ *Ztschr. angew. Chem.*, 1898, 125.

‖ *Journ. Chem. Soc.*, 1904, 85, 1.

into a 300 c.c. flask having a tight stopper and fitted with a funnel and side tube, 20 grams of potassium dichromate and 80 c.c. of dilute sulphuric acid (1 : 4) added and the mixture allowed to remain for 18 hours. A further quantity of 10 grams of potassium dichromate and 50 c.c. of sulphuric acid mixed with an equal volume of water are now added, and the contents of the flask heated to the boiling point for about 10 minutes, the evolved carbon dioxide being swept out of the apparatus by a current of air and collected in weighed soda lime tubes. Under these conditions each gram of ethyl alcohol was found to yield about 0.01 gram of carbon dioxide. The remaining carbon dioxide found is calculated as being derived from the complete oxidation of methyl alcohol. This method is used for the quantitative determination of methyl alcohol in the Government Laboratory, London.

Amyl Alcohols.

The amyl alcohols are the principal constituents of fusel oil, and most of the methods proposed for the determination of fusel oil in distilled liquors are essentially attempts to estimate the amyl alcohols. In order to separate the amyl alcohols from the relatively large amounts of ethyl alcohol ordinarily present, advantage is taken of the fact that the former are much more soluble in chloroform than is the latter, so that on shaking a small amount of chloroform with a distillate containing about 30 per cent. of alcohol practically all of the amyl alcohols and only a little of the ethyl alcohol, pass into the chloroform layer. The amount of amyl alcohol removed by the chloroform is usually estimated either :

1. By measuring the increase in volume of the chloroform layer (Roese's method).

2. By oxidizing with potassium dichromate and determining the amount of valerianic acid produced (Marquardt's method).

Neither method gives very satisfactory results. The Association of Official Agricultural Chemists * has adopted the Roese method as carried out by Windisch. Allen † recommends a modification of the Marquardt method.

Methods of Stating Strength of Alcohol Solutions.

The most satisfactory method of expressing the amount of alcohol in a solution is in terms of percentage by weight. The use of

* Bull. 65, Bur. Chem., U. S. Dept. Agriculture.

† Commercial Organic Analysis, Vol. I, p. 154.

the "percentage by volume" is, however, probably more common, while frequently the results of an analysis of alcoholic liquor are stated in grams of alcohol per 100 c.c. of sample.

For revenue purposes, both in the United States and Great Britain, the strength of alcoholic liquors is expressed in terms of "proof spirit," but the term has different meanings in the two countries. *American proof spirit* contains 50 per cent. of alcohol by volume, corresponding to about 42.7 per cent. by weight. *British proof spirit* is defined by Parliament as having such a density that at 57° F., thirteen volumes shall weigh the same as twelve volumes of water at the same temperature. This corresponds to about 49.2 per cent. by weight.

The U. S. Pharmacopeia authorizes the designation "*Absolute Alcohol*" for that which contains at least 99 per cent. by weight and "*Alcohol*" for that containing 91 per cent. by weight or 94 per cent. by volume.

"*Spirit*" of the German Pharmacopeia contains about 86 per cent. of alcohol by weight.

"*Rectified Spirit*" of the British Pharmocopeia has 84 per cent. by weight and British "*Methylated Spirit*" consists of nine parts of rectified spirit to one part of commercial "wood spirit" or "wood naphtha," the latter containing, according to recent observations of Thorpe and Holmes, from 72 to 80 per cent. of methyl alcohol by volume.

GLYCEROL.

Glycerol is a colorless, odorless, viscous liquid of sweet taste and neutral reaction, miscible in all proportions with water and with alcohol. It also dissolves in mixtures of alcohol and ether, but is only very sparingly soluble in pure ether * and practically insoluble in chloroform, carbon disulphide and benzene. The specific gravity of pure glycerol at 15° referred to water at the same temperature, is variously stated at from 1.265 to 1.2677. Anhydrous glycerol boils at about 290°, but evaporates rapidly at lower temperatures (160° or over) and the evaporation is greatly accelerated by the presence of a small amount of water. When kindled, glycerol burns with a blue flame and leaves no carbonaceous residue.

These properties together with the fact that it yields acrolein when heated with acid potassium sulphate, are usually sufficient for

* According to Lewkowitsch, one part of glycerol of 1.23 sp. gr. dissolves in about 500 parts of ether.

the identification of glycerol when in a fairly pure and concentrated state.

Glycerol is a good solvent for many substances, both organic and inorganic, and its presence often increases their solubility in aqueous and alcoholic solutions. This fact and the difficulty of distilling without loss * make it troublesome to separate glycerol as a pure aqueous solution as is done in the determination of alcohol. The method to be followed in removing the other substances which may interfere with the determination will depend upon the nature of the sample. The final determination is usually made in one of three ways: (1) By oxidation with potassium dichromate. (2) By the formation of triacetin. (3) By separation and weighing.

The first and second methods will be described as applied to crude or commercial glycerins, the third as applied to wines.

Determination by Oxidation.

While other methods of determining glycerol by oxidation have been proposed, that of Hehner † is the one now generally used. It is based on the fact that glycerol can be quantitatively oxidized to carbon dioxide and water by heating with potassium dichromate in the presence of sulphuric acid.

Reagents. — (1) Strong solution of potassium dichromate made by dissolving 74.64 grams of the pure salt (previously pulverized and dried at 130°–135°) and diluting the solution to one liter. (2) Weak solution of dichromate made by diluting 100 c.c. of the strong solution to one liter. (3) A solution containing about 240 grams of ferrous ammonium sulphate and about 10 c.c. of concentrated sulphuric acid per liter.

Apparatus which is to come in contact with the dichromate solution must be very carefully cleaned in advance with a solution of dichromate in strong sulphuric acid.

Determination. — Weigh such an amount of the sample as will contain about 1.5 grams of actual glycerol into a 100 c.c. flask, dilute to about 10 c.c., add 0.5 to 1.0 gram silver oxide and let

* An approximate separation of glycerol from dissolved solids can easily be made by distilling with steam. At sufficiently reduced pressure the steam distillation may be carried on with very little loss of glycerol, this process being used on a large scale as a means of refining commercial glycerin. The necessary apparatus is, however, not always available in the laboratory and the completeness of distillation and recovery of the glycerol has not yet been definitely settled.

† *Journ. Soc. Chem. Ind.*, 1889, 8, 4.

stand for ten minutes, shaking frequently; then add basic lead acetate in slight excess and fill to the mark. After thorough shaking, filter through dry paper, discarding the first few c.c.; transfer 25 c.c. of the filtrate to beaker, add 30 c.c. of a mixture of equal volumes of sulphuric acid and water and then run in 50 c.c. of the stronger solution of potassium dichromate, measuring the volume with the greatest possible accuracy. Cover the beaker with a watch glass and place it in boiling water for two hours. During this time the exact strength of the ferrous sulphate solution is determined by titration against the dichromate. At the end of the two hours remove the beaker from the boiling water, add 100 c.c. water and titrate the excess of dichromate remaining. Each cubic centimeter of the stronger dichromate solution which has been reduced indicates the oxidation to carbon dioxide and water of 0.01 gram of glycerol.

Notes. — The treatment of the sample with silver oxide precipitates chlorides and oxidizes any aldehydes which may be present. Basic lead acetate precipitates proteids, resinous matter, and the higher fatty acids. Hehner supposed that these two reagents would remove all impurities likely to be found in crude glycerins which could be oxidized by dichromate under the conditions given. In a number of cases, however, genuine crude glycerins have given high results by this method, doubtless because they contained oxidizable impurities not removed by silver oxide and basic lead acetate.

As the oxidizing dichromate solution is a strong one, it must not only be measured with the greatest care but it should always be shaken before using in order to wash down any drops of water which may have evaporated from the solution and condensed on the inner surface of the bottle. Attention must also be paid to the temperature at the time of measuring. According to Hehner this solution expands 0.05 per cent. for each increase of one degree C.

As the method is ordinarly described, the excess of dichromate remaining after the oxidation of the glycerol is reduced by adding a known amount of the ferrous ammonium sulphate solution and the excess of the latter titrated by the weaker dichromate. The green color of the solution makes the end reaction with ferricyanide somewhat difficult to detect and it will usually be found more satisfactory to determine the excess of the stronger dichromate by direct titration with the ferrous solution. Then if the end point

is accidentally overrun, add quickly 5 or 10 c.c. of the weak (equal to 0.5 or 1.0 c.c. of the strong) dichromate and continue titrating with the ferrous solution until the blue reaction with ferricyanide appears.

Determination by Acetylation.

On heating with acetic anhydride glycerol is completely converted into the triacetate. This is the basis of the acetin method of Benedict and Cantor * which is applied to commercial glycerins as follows:

Weigh 1 to 1.5 grams of the sample (which must not contain more than 30 to 40 per cent. of moisture) into a flask, add 3 to 5 grams of recently fused sodium acetate and 7 to 10 c.c. acetic anhydride and boil under a reflux condenser for one and one-half hours. Allow to cool, pour 50 c.c. of water into the flask through the condenser and heat gently with the condenser still attached until the liquid begins to boil and the oily layer of triacetate goes into solution. Remove the condenser, add phenolphthalein and carefully neutralize with 5 per cent. sodium hydroxide solution. Care must be taken to avoid any excess of alkali at this point as the triacetate is easily hydrolyzed. Shake the solution well to avoid any local excess of alkali during the neutralization, and stop adding alkali as soon as the solution changes to a reddish-yellow color. If the solution were made sufficiently alkaline at this point to show a full pink color, the final result would be too low.

To the neutralized solution add 25 c.c. of a 10 per cent. solution of sodium hydroxide (accurately measured by a pipette), boil for 10 to 15 minutes and titrate the excess of alkali with accurately standardized acid. At the same time determine the exact strength of the alkali solution by measuring out another portion of 25 c.c. with the same pipette and titrating with the same acid, using phenolphthalein as indicator. The difference between the two titrations shows the amount of alkali consumed in saponifying the triacetate and from this the amount of glycerol is calculated, one molecule of glycerol being equivalent to three molecules of sodium hydroxide.

Notes. — If sufficient care is taken to prevent any of the acetin from being lost by evaporation or saponified during the neutralization of the excess of acetic anhydride, the results by this method are very accurate. If these precautions are not carefully observed

* *Ztschr. angew. Chem.*, 1888, 460.

the results are likely to be somewhat low. Practically pure glycerol should give the same results by acetylation as by oxidation. Crude glycerins often give much higher results by the latter method. In such cases the acetin method should be repeated with special attention to the precautions already mentioned and to the moisture present in the sample and the sodium acetate used. Unless the sample contains over 60 per cent. of glycerol and the sodium acetate is strictly anhydrous, the formation of the triacetate is likely to be incomplete. When carried out under the proper conditions the results by the acetin method should be preferred to those by the dichromate because the impurities of crude glycerins are more likely to vitiate the latter than the former method. In cases where other oxidizable substances are absent or can be entirely removed, it is a good plan to make a determination by each method and average the results obtained. For dilute solutions the dichromate method, if applicable, is much more convenient because the acetin method cannot be applied until after the glycerol has been concentrated by careful evaporation.

Determination by Separation and Weighing.

For the estimation of glycerol in fermented liquors where it occurs mixed with relatively large amounts of alcohol, sugar, organic acids and resinous, nitrogenous and other "extractive" matters, the plan usually followed is to evaporate off the greater part of the alcohol and water and then treat with lime and after further evaporaton take up the glycerol with strong alcohol, leaving the greater part of the extractive matters in the residue. The substances, other than glycerol, which pass into the alcohol solution are largely precipitated by the addition of ether and the alcohol-ether solution is then evaporated.

The details of the process as adopted by the Association of Official Agricultural Chemists* for the determination of glycerol in wine are as follows:

Evaporate 100 c.c. of wine† in a porcelain dish on the water

*Bull. 65, Bur. Chem., U. S. Dept. Agriculture.

†With wines whose extract exceeds 5 grams per 100 c.c., heat to boiling in a flask the portion to be used in the determination of glycerol, and treat with successive small portions of milk of lime until it becomes, first, darker, and then light in color. When cool, add 200 c.c. of 96 per cent. alcohol (sp. gr. 0.812), allow the precipitate to subside, filter, and wash with 96 per cent. alcohol. Evaporate the filtrate to about 10 c.c., add about 5 grams of sand and from 1.5 to 2 c.c. of milk of lime, and proceed as directed above.

bath to a volume of about 10 c.c. and treat the residue with about 5 grams of fine sand and with from 1.5 to 2 c.c. of milk of lime (containing about 40 per cent. of calcium hydroxide or 30 per cent. of calcium oxide) for each gram of extract present, and evaporate almost to dryness. Treat the moist residue with 5 c.c. of 96 per cent. alcohol (sp. gr. 0.812), remove the substance adhering to the sides of the dish with a spatula, and rub the whole mass to a paste, with the addition of a little more alcohol. Heat the mixture on the water bath, with constant stirring, to incipient boiling, and decant the liquid into a flask graduated at 100 and 110 c.c. Wash the residue repeatedly by decantation with 10 c.c. portions of hot 96 per cent. alcohol. Cool the contents of the flask to 15°, dilute to the 110 c.c. mark with 96 per cent. alcohol, and filter through a folded filter. Evaporate 100 c.c. of the filtrate to a sirupy consistency in a porcelain dish, on a hot, but not boiling, water bath, transfer the residue to a small glass-stoppered graduated cylinder with 20 c.c. of absolute alcohol, and add three portions of 10 c.c. each of absolute ether, mixing after each addition. Let stand until clear, then pour off through a filter, and wash the cylinder and filter with a mixture of one part absolute alcohol to one and one-half parts of absolute ether, pouring the wash liquor also through the filter. Evaporate the filtrate to a sirupy consistency, dry for one hour at the temperature of boiling water, weigh, ignite, and weigh again. The loss on ignition increased by one-tenth gives the glycerol expressed in grams per 100 c.c.

Notes. — When a mixture of glycerol and water is concentrated at about the boiling point of the latter, water evaporates without any considerable loss of glycerol until the latter becomes quite highly concentrated. The point at which glycerol begins to be lost depends upon a number of conditions such as temperature, the depth of the layer, etc., but some loss always occurs in expelling the last of the water. The same is true with regard to the concentration of alcoholic solutions though the loss here is less as glycerol is less volatile with alcohol than with water vapor. On the other hand the glycerol obtained by this method has other impurities than ash, and these are calculated as glycerol. For detailed tests of the method see the work of Neubauer and Borgmann on wines * and that of Clausnitzer on beers.†

* *Ztschr. anal. Chem.*, 1878, 17, 442.

† *Ibid.*, 1881, 20, 58.

See also — Friedebérg : Ueber Glycerinbestimmung in vergohrenen Getränken, Dis-

Examination of Commercial Glycerol.

Commercial glycerol (or "glycerin") always contains water, and all but the best "chemically pure glycerol" contains appreciable amounts of impurities derived from the original fat or from the saponifying agents. The tests to be applied and the allowable limits of impurity will depend upon the purpose for which the glycerin is to be used. The quantitative determinations most commonly required are: specific gravity, carbonaceous residue, ash and salt. The higher grades of glycerin must also be practically neutral and show no turbidity due to fatty acids when the sample is diluted with water, and hydrochloric acid added.

Additional tests and specifications for pharmaceutical glycerin will be found in the *U. S. Pharmacopeia* and *Dispensatory*.

Glycerin used for the manufacture of nitroglycerol need not be colorless but must have a high degree of purity as shown by the following quantitative determinations.

Specific Gravity.

The viscosity of glycerol and the fact that when highly concentrated it is quite hygroscopic make it necessary to use the greatest care in this determination. Hehner * recommends the Sprengel tube and Lewkowitsch † the ordinary specific gravity bottle. It is usually more convenient to take the specific gravity by using the hydrostatic sinker with the analytical balance. For this purpose the Reimann sinker graduated for 15° is very convenient. The glass body encloses a thermometer (usually graduated from 0° to 27°) and is of such size that when immersed it displaces 5 (or sometimes 10) grams of water at 15°. This calibration should be tested for each sinker as it is received from the dealer, by suspending it over the pan of the analytical balance, finding its weight in air and then determining its weight when suspended in the same position but immersed in recently boiled distilled water at 15°. This is easily done by placing a bridge over the balance pan and on this bridge a small cylinder containing enough water to cover the sinker to a depth of about 1 cm. The sinker should hang in the center of the cylinder and the diameter of the latter should

sertation, Berlin, 1890. Schaumann: Bestimmung von Glycerin im Wein; Dissertation, Erlangen, 1891.

* *Journ. Soc. Chem. Ind.*, 1889, 8, 4.

† Oils, Fats and Waxes [3d Ed.], p. 1104.

be about three times that of the former. Having found the weight of water displaced, remove and dry the sinker, replace the cylinder of water by one filled to the same depth with the sample of glycerin to be tested and weigh the sinker suspended in the glycerin at 15°. The loss of weight in glycerin divided by that in water shows the specific gravity of the former referred to water at the same temperature.

If the sample consists of glycerol and water with only insignificant amounts of impurities, the specific gravity serves as a measure of the concentration. This method is, however, considerably less accurate than in the determination of alcohol because the specific gravity of pure anhydrous glycerol is less accurately known than that of absolute alcohol. The most generally accepted tables of specific gravities of glycerol solutions are those of Lenz* and Nicol.† Reduced to 15.5° and 15°, the values for concentrated solutions as found by these observers are:

Glycerol Percent.	Specific Gravity at 15.5° Lenz.	Specific Gravity at 15° Nicol.	Glycerol Percent.	Specific Gravity at 15.5° Lenz.	Specific Gravity at 15° Nicol.
100	1.2674	1.26596	87	1.2327	1.23128
99	1.2647	1.26335	86	1.2301	1.22855
98	1.2620	1.26072	85	1.2274	1.22583
97	1.2594	1.25809	84	1.2248	1.22310
96	1.2567	1.25547	83	1.2222	1.22038
95	1.2540	1.25285	82	1.2196	1.21766
94	1.2513	1.25021	81	1.2169	1.21493
93	1.2486	1.24756	80	1.2143	1.21221
92	1.2460	1.24487	79	1.2117	1.20949
91	1.2433	1.24217	78	1.2090	1.20677
90	1.2406	1.23945	77	1.2064	1.20404
89	1.2380	1.23673	76	1.2037	1.20131
88	1.2353	1.23400	75	1.2011	1.19857

It has also been proposed to apply a correction for the influence of salt on the specific gravity and use the corrected figure as a rough measure of the glycerol present in crude glycerins.‡

If the percentage of glycerol indicated by the specific gravity is less than that shown by the dichromate method, the presence of oxidizable compounds of lower density than glycerol is indicated. Thus a sample of "light" glycerin examined by Noyes and Watkins§ was found to contain about 38 per cent. of trimethylene

* Recommended by Hehner, *Journ. Soc. Chem. Ind.*, 1889, 8, 4.

† U. S. Dispensatory (18th Ed.), p. 657.

‡ Richardson and Joffe, *Journ. Soc. Chem. Ind.*, 1898, 17, 330.

§ *Journ. Amer. Chem. Soc.*, 1895, 17, 890.

glycol. Since this glycerin was obtained largely from refuse house fat, the glycol was probably formed by spontaneous saponification and subsequent fermentation of the glycerol in the impure rancid fat. This glycol has also been found in considerable quantity in the "tank liquor" separating from the fat before saponification* and is probably not an uncommon impurity, especially in glycerin obtained from refuse fats.

Samples containing glycol would, of course, yield lower results by the acetin than by the dichromate method.

Carbonaceous Residue and Ash.

Weigh about 50 grams of glycerin into a 50 c.c. platinum dish, heat cautiously over a Bunsen burner until the sample ignites, remove the burner and allow the glycerol to burn away, being careful that the dish is not exposed to draughts. When burning ceases, transfer the dish at once to a desiccator and when cool weigh quickly, as the residue is apt to be hygroscopic. After weighing the carbonaceous residue, burn to whiteness and weigh the ash.

Sodium Chloride.

Weigh 50 to 100 grams of sample, dilute with twice its volume of water, add a few drops of potassium chromate solution and titrate with standard silver nitrate, preferably tenth-normal or of such strength as to be equivalent to a one per cent. solution of sodium chloride.

Specifications for Dynamite Glycerin.

The following specifications are furnished by the firm of Wm. F. Jobbins as representing the requirements of a majority of the nitroglycerol manufacturers in the United States at the present time (1904).

Specific Gravity at 15°, not less than 1.2625.

Carbonaceous Residue (including ash) and *Ash* as determined by the method given above, must not exceed 0.03 per cent. and 0.01 per cent. respectively.

Sodium Chloride determined as above must not exceed 0.01 per cent. and is usually very much less than this amount.

Total Acid Equivalent ("*Fatty Acids*") is determined as follows: Dilute the sample with twice its volume of water, add a few drops of phenolphthalein solution and a decided excess of standard

* Twitchell: *Journ. Amer. Chem. Soc.*, 1895, 17, 891.

sodium hydroxide; boil five minutes and then titrate the excess of alkali by standard acid. The glycerin must not consume more than 0.10 per cent. of its weight of sodium hydroxide in this test.

For a fuller discussion of the examination of "dynamite glycerin," see a paper by Barton in the *Journal of the American Chemical Society* (1895, 17, 277).

Detailed information on the testing of "dynamite glycerin" and other grades of commercial glycerol will be found in Lewkowitsch's "Oils, Fats and Waxes," and in Allen's "Commercial Organic Analysis."

METHODS OF RENEWING OLD TIMBERING AT THE DIVES-PELICAN MINE, SILVER PLUME, COLORADO.

By JAMES F. McCLELLAND.

The Dives-Pelican Mine is one of the oldest in Clear Creek County, having been in operation almost continuously for more than thirty years. In the early history of this property, the high cost of labor, transportation, supplies, etc., made it impossible to mine at a profit any but high grade deposits of ore. Practically the same policy has been followed up to the present time, with the results that the old stopes contain large quantities of ore, of too low a grade to ship directly to the smelter. Recently there has been a combination of several properties and it is proposed to make the ore in the old stopes the basis of large-scale mining operations.

Many of the old workings have been abandoned for a long time and have caved in. In most cases the drifts were driven in a soft porphyry which swells and shells off on exposure to the air, making it necessary to support the walls as well as the back of the drift. Much preliminary work, in the nature of reopening and retimbering the old workings has been necessary before actual mining operations can begin, and this work seems unusual and interesting enough to warrant its description.

Retimbering Old Drifts.— As mentioned above, the walls of the drifts require support. They are rarely strong enough to carry stulls and the stopes are supported in most cases by ordinary three-quarter sets. The standard set with its dimensions and framing is shown in Fig. 15. Round timber is used exclusively and is mostly native spruce obtained in the vicinity of Silver Plume. The posts of the sets are usually ten inches, and the caps twelve inches in diameter. No sills are used; the posts are either braced to the track as shown in Fig. 15, or else the feet are kept apart by a six-inch timber spiked in place on a level with the ties and extending clear across the drift (Fig. 5). The sets are lagged with poles from four

inches to six inches in diameter. The side lagging is placed as shown in Fig. 1, and the space behind the pieces filled with broken rock. The timber in the main sets has an average life of from four to six years, but the lagging does not last as as long this. The pressure of the walls and the overlying ore is made evident by the fact that old drifts which are still open are from six inches to a foot lower and narrower than they were originally.

Before an old set can be taken out, the lagging around it and on each side of it must be replaced. At the same time the drift is restored to its original cross section. The lagging is replaced one stick at a time, beginning with that in the roof. Usually the weakest of the old poles is pulled down first, with a pick or bar. Some broken rock will fall at the same time, but generally there are enough large lumps of ore in the stope above to wedge and hold for a short time. If necessary, the hole made in this way is enlarged with a gad and a new lagging pole is inserted, resting at one end on top of the lagging of the set last replaced, and at the other on short blocks set on the cap of the old set (*P*, Fig. 1). The adjoining lagging pole is then pulled down and replaced in the same manner, the process being repeated until the whole roof has been relagged. This method of putting in the lagging gives the completed work a peculiar appearance, as the lagging poles are inclined downwards instead of upwards as is ordinarily the case.

The side lagging is taken out and renewed in a similar way. As a general rule this work begins at the top of the drift and proceeds downward, but the presence of fissures and loose slabs of rock may reverse this order. Much work with a gad is usually necessary to get sufficient room to set the side lagging far enough back so that they will take a new set. The forward ends of these lagging poles are blocked against the old set as shown in Fig. 3.

When new lagging poles have been put in place all around the drift, a false set (Figs. 1 and 2) is erected about six inches behind the old set. This is a three-quarter set, made of six inch timber, with its outside dimensions slightly greater than those of the standard set. The posts are sunk in hitches six or eight inches deep and are braced to the track. This set is also braced back to the

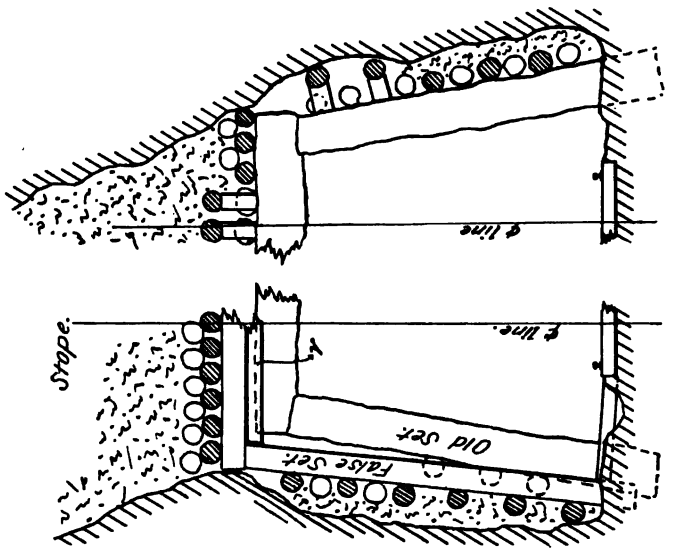


FIG. 2. Half section on *AB*. FIG. 3. Half section on *CD*.

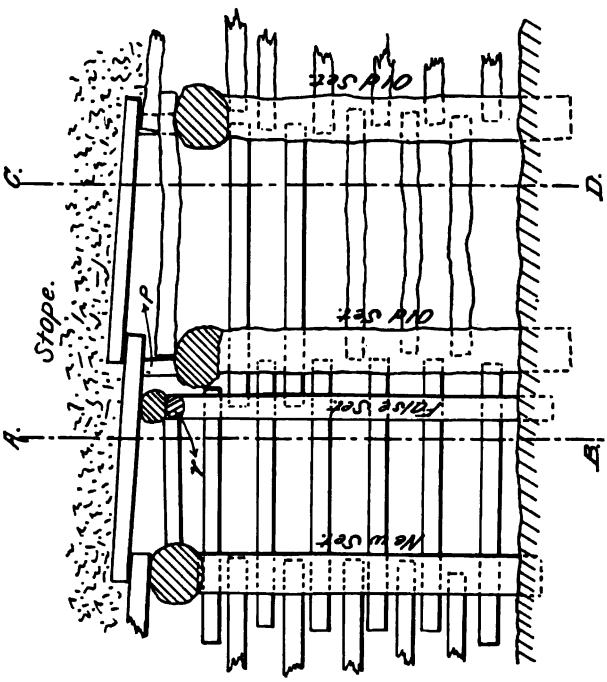


FIG. 1. Longitudinal Section through Drift with Lagging Partially Replaced.

last new set to prevent its overturning under pressure (Fig. 1). The false set is used over and over again, and, for convenience in erection and removal, a false cap (*r*, Figs. 1 and 2) is used to brace the heads of the posts apart, instead of the notch used in the regular set. If the work is carried out properly the cap of the false set fits snugly against the new top lagging and the posts are driven into place with a sledge. If the top lagging poles are too low they may often be raised by putting a drill column under the cap of the false set and using it as a jackscrew. The drill column is of great service also in placing the timbers of the main sets and for many other purposes.

The side lagging is then wedged firmly against the posts of the false set, and the lagging in front of the old set replaced in exactly the same manner as described above. The rear ends of the side lagging poles, however, must be caught by the posts of the false set as shown in Fig. 1, so that these lagging poles are cut longer than would otherwise be necessary.

When this has been completed, the old set is knocked out and the new one erected in its proper position. The side lagging is then driven ahead to a firm bearing on the new set, and the false set is removed. The same cycle of operations is repeated to renew the next set.

The details of carrying out this work are varied to meet different conditions, as, for instance, in replacing half-sets instead of three-quarter sets. Where the ends of the lagging butt on top of the cap instead of overlapping, two false sets are necessary, one on each side of the old set, but otherwise the operations are the same.

Quite a little broken rock and ore will fall into the drift in doing this kind of timbering. This is often a convenience, since it gives the men something to stand on while replacing the back lagging. Its amount varies greatly with the character of the material encountered, but with careful work under ordinary conditions it should not exceed three tons per set. Part of this broken material is used as a filling behind the side lagging.

A timberman and his helper will average about one set per day of eight hours. The cost of this work per set replaced is approximately as follows:

Timberman	$2.75
Helper	2.50
Timber (including framing) .	4.00
Tramming, mucking, etc. . .	.70
Total	$9.95

Since the sets are 4 feet 8 inches apart, the cost is about $2.15 per foot of drift retimbered.

Reopening Caved Drifts.—This work is more difficult and dangerous than that of replacing old timber. The simplest case occurs when the back of the drift will stand unsupported for a short time. Enough of the broken ore is removed to make room for a new set, which is then put in place, braced, and lagged. The top lagging poles are put on first. In many instances however

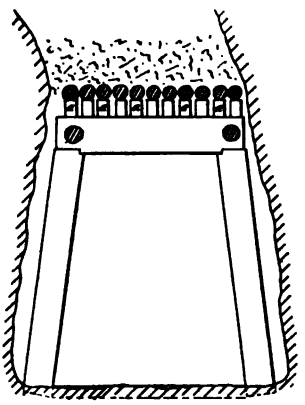


FIG. 5. Section on *AB*.

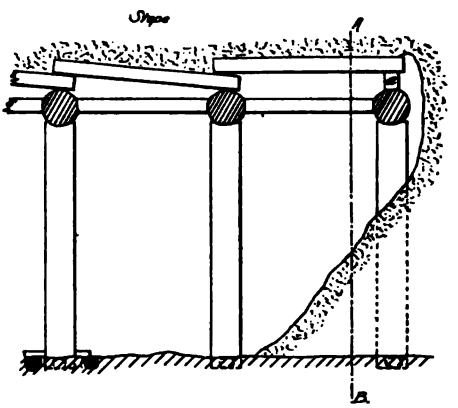


FIG 4. Longitudinal Section through Drift showing Timbering ready to begin Spiling (side lagging omitted).

the ore is dry and shows a strong tendency to run. It then becomes necessary to resort to "spiling."

The timbering is first brought up as near as possible to the caved portion of the drift in the manner already described, and the forward ends of the lagging poles are blocked up on the last set as shown at *a*, Figs. 4 and 5. The blocks used are sawed from lagging poles and are about 6 inches long. Smooth lagging poles, 4 or 5 inches in diameter, and roughly sharpened at one end, are used for spiling poles. The point of one of these is held against one of the blocks (*a*, Fig. 5), and the pole is driven forward with a

sledge. This of course knocks out the block but the spiling pole supports the lagging above. All of the blocks are replaced in the same way, the spiling being driven ahead into the caved material as far as possible. Wedges (*b*, Fig. 6) are inserted to keep the spiling at a proper inclination. Under the protection of these spiles, some of the caved material is removed, the spiles are driven further ahead, and a false set (*c*, Fig. 6) is erected from two to three feet ahead of the main set. The work then has the appearance shown in Fig. 6. Next, the spiles are driven home and the new set is erected as shown in dotted lines. The next spiling poles can then be started under the cap of the false set and over the cap of the main set.

In carrying out this work, care must be taken to keep all of the spiling poles even and at the same inclination. They should be

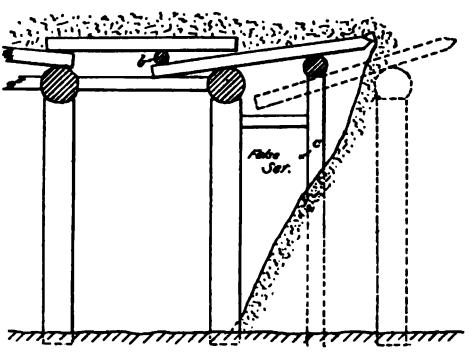


FIG. 6. Longitudinal Section through Drift (side lagging omitted).

given sufficient pitch to insure plenty of room above the main set for the insertion of the next series of spiling poles. The poles themselves must be cut longer than the ordinary lagging pole. Where the sets are placed 4 feet 8 inches center to center, a six-foot spiling pole is not too long.

The presence of large rocks may cause a great deal of trouble. Where possible the spiling poles are driven over a large rock. If this can not be done, the rock either must be split up with a gad, or a sufficient amount of the caved material removed from underneath to allow it to fall.

As a general rule the walls of the drift do not require spiling and they are lagged in the ordinary way, after the roof is completed, and the new set in place. If necessary they may be spiled

in a similar manner. For the sake of clearness the side lagging has not been shown on the drawings.

An interesting variation of this method is shown in Figs. 7 and 8. Here the back of the drift caved unexpectedly just after a new half set had been put in place and lagged. The caved material ran freely and spiling became necessary. The pressure of the overlying ore was so great, however, that the ends of the lagging poles could not be raised to give room enough to start spiling poles. This difficulty was overcome by cutting away a portion of the ends of two adjacent lagging poles, directly over the cap. A spiling pole was then driven through the hole formed in this way (Fig. 7). The next lagging and the remaining portion of the first lagging were then cut away in the same manner, and a second spile was driven in alongside of the first. Fig. 8 is a photograph showing the ends of three spiles which have been put in place in this way. By repeating the process, spiles were driven in across the whole roof. These spiling poles were cut so long that their rear ends projected behind the cap, and supported the forward ends of the lagging, thus avoiding any weakness due to cutting the lagging away where they rested on the cap. The same device is resorted to in repairing caves of one or two sets in heavy ground.

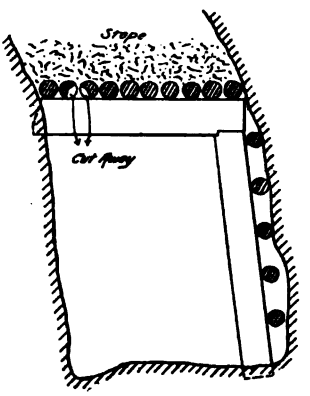


FIG. 7.

The method of spiling as above described answers satisfactorily for the ordinary conditions encountered, but occasionally ground is met with which runs so freely that the face of the drift must be supported before room enough can be obtained to erect the new set. Breast boards are then used to hold back the face as shown in Figs. 11, 12, 13 and 14. In a particular case observed, the hanging wall was strong enough to carry timber in a hitch, while the foot wall was much softer. Spiling poles, seven feet long, were driven in and a false set (*e*, Fig. 9) was erected as usual. As the poles were driven past the false set, no attempt was made to excavate the whole face; only a small portion of the caved material directly under the spiles was taken out. A six-inch timber (*a*,

Figs. 9 and 10) was then put in place, with its ends supported by hitches cut in the walls. Near the foot wall end a post, *b*, was set up and given a firm footing on a two-inch block imbedded in the ore. This post was braced back to the false set. More of the caved material was then removed and the pole, *c*, Figs. 11 and 12, was put in and braced back to the post *b*. The ends of this pole

FIG. 8.

also rested in hitches. Breast boards of one-inch plank, ten inches wide and twenty-four inches long were driven into the caved ore behind the pole *c*, as shown in Figs. 11 and 12. These boards served to support the face sufficiently to allow excavation to proceed to the point *d*, where a second pole and series of breast boards could be put in.

At this point a second post similar to *b*, but longer, was set up under the timber *a*, near the center of the drift, and the poles *c* and *d* were braced to it. The post *b* was then removed and a longer one substituted for it. By repeating these operations, the whole

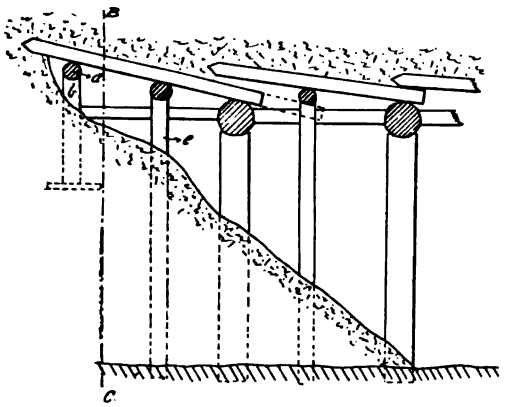


FIG. 9. Longitudinal Section through Drift (side lagging omitted).

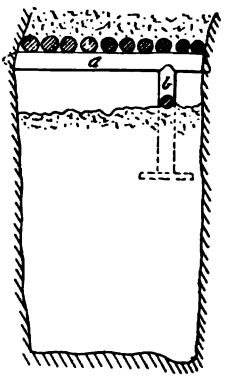


FIG. 10. Cross-section *BC*.

face of the drift was opened up and the new set was erected just in front of the breast boards. Fig. 13 is a photograph of the face showing the false set and the pieces *a*, *c* and *d*, while Fig. 14 shows

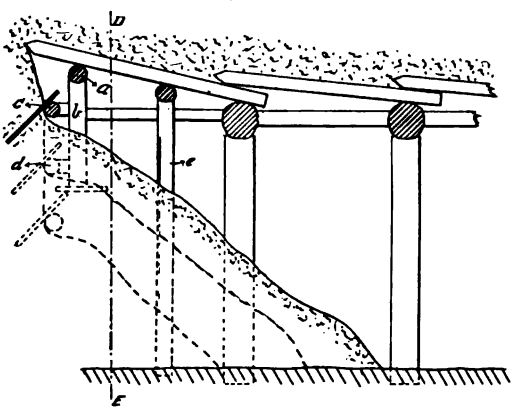


FIG. 11. Longitudinal Section through Drift (side lagging omitted).

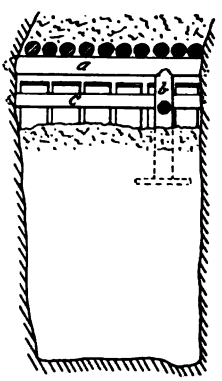


FIG. 12. Cross-section *DE*.

the appearance of the work just after the posts of the new set have been put in place.

The presence of old and decayed timber in the caved ore is often

of material assistance in preventing the ore from running while carrying out the work. Obviously the method may be modified for use where both walls are too soft to carry timbers in hitches.

It is impossible to estimate the cost of doing work like spiling and breast boarding, owing to the great irregularity in the conditions encountered. A set may sometimes be put up in a single day, while another will take a week for its completion. In all cases,

FIG. 13.

however, this work is much more expensive than the replacement of old timber.

Chutes for Drawing Ore from Old Stopes. — The old mill holes in the mine stopes have caved in, and are useless. For drawing the ore, chutes have been erected at intervals of about 25 feet along the drifts. These are peculiar in that they are put in after the regular

drift timbering has been completed. The chutes are built between the sets as shown in Figs. 15 and 16. When completed three or four lagging poles directly overhead are either withdrawn or cut away.

The details of construction vary in different cases. Figs. 15 and 16 show a chute built under three quarter sets, and Fig. 17 shows

FIG. 14.

the form used with stull timbering. The gate is represented in section in Fig. 18. It is convenient and easily operated. The use of two gate boards gives good control over the passage of the ore and allows large rocks to be easily extracted. In order to facilitate the raising of the gate boards, the front of the chute is made about an inch wider at the top than at the bottom (Fig. 16).

Many of these chutes were erected and used to obtain large samples of the ore in the old stopes, while the property was being sampled.

Raising through an Old Stope.— Fig. 19 shows a longitudinal section through a raise which was put up through an old stope to

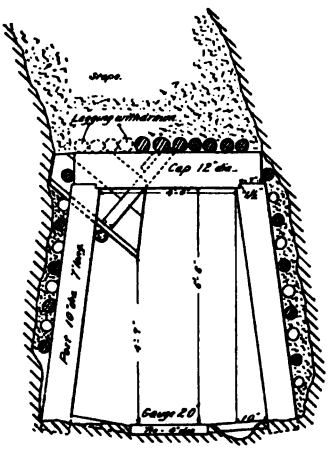


FIG. 15. Cross-section on *LM.*

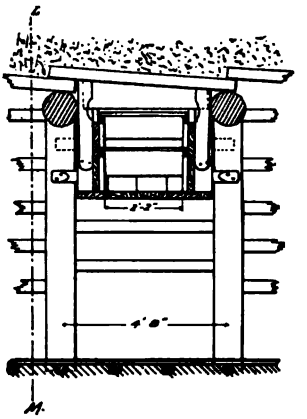


FIG. 16. Longitudinal Section through Drift, showing Chute.

reestablish communication with some abandoned workings. The broken ore at this point was well packed in the stope and would

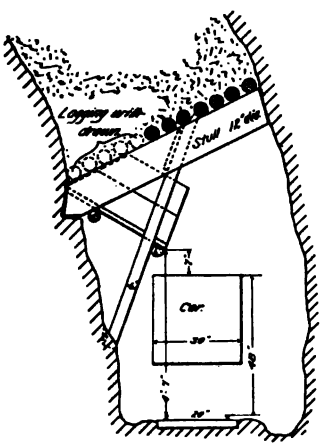


FIG. 17. Cross-section through Drift, showing Chute built in connection with Stull Timbering.

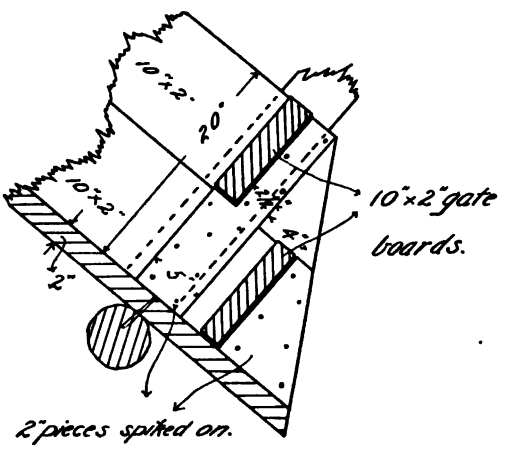


FIG. 18.

not run in very large amounts. When the raise had been carried up about fifty feet, a solid rock pillar was unexpectedly encoun-

tered, necessitating the change in direction shown in Fig. 19. The distance between the foot and hanging walls varied from two to four feet, and the walls themselves were fairly strong.

The timbering consists of three rows of short stulls (called spreaders) about four feet apart and set in hitches as shown in Fig.

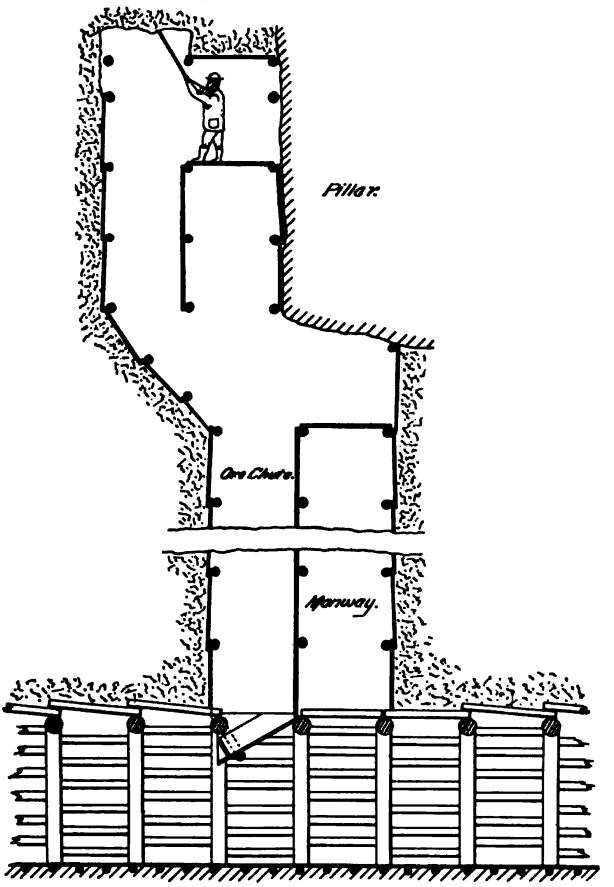


FIG. 19. Longitudinal Section throngh Raise.

21. These divide the raise into two compartments, one of which is used for a manway and the other for an ore-chute. Two inch plank is spiked to the middle row of spreaders to form a tight partition between the compartments. Plank is also used for lagging the outside spreaders (Fig. 20).

Only one half of the face of the raise is advanced at one time

The last spreaders on the other side are covered with planks, thus forming a roof, under the protection of which a man can stand and work. Most of the actual excavation is done with a bar, the loose material falling into the chute below. When the face has been advanced about two feet a couple of temporary spreaders (*a*, Fig. 20) are put in and covered with plank. The miner then stands under these and bars down the face on the other side of the raise. The

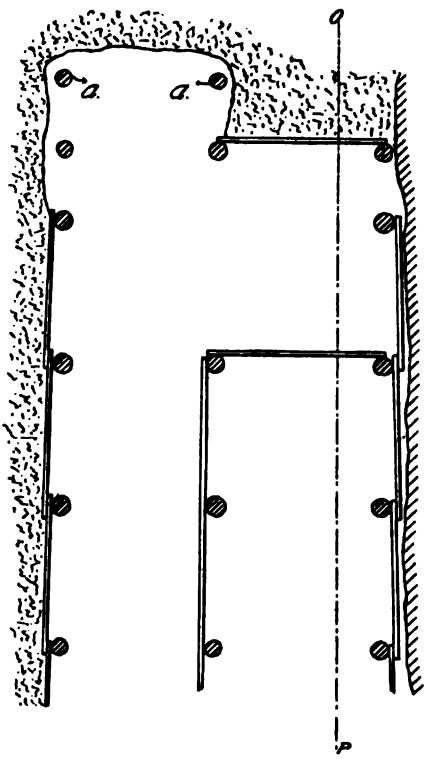


FIG. 20. Longitudinal Section through Raise.

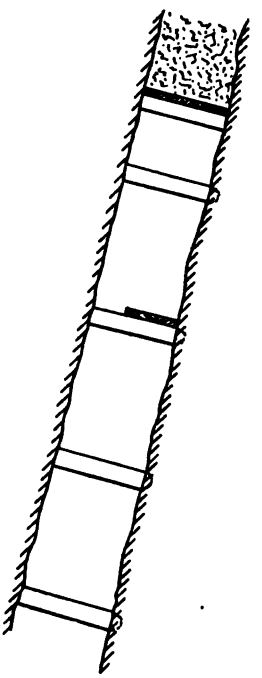


FIG. 21. Cross-section on *OP*.

permanent spreaders are put in when the raise has advanced far enough, and the lagging and partition are kept up as near as possible to the face.

This work is dangerous and requires a high degree of skill on the part of the miner. The ore in the chute was kept as low as possible, so that in case of a sudden cave of a large amount of material the chute would not fill up entirely and imprison the men.

A METHOD OF SOLVING A THREE-CENTERED COMPOUND CURVE WITH TRANSITIONS.

By SHELDON SMILLIE, E. M.

In the summer of 1902 while running a short section of railroad, at the Summer School of Surveying, Camp Columbia, one of the squads had to run a three-centered compound curve, as such a curve fitted the ground, which was around the side of a steeply sloping hill, exactly. The work required, for practice, that all sudden changes of direction should be eased, or, in other words, approached by transition curves. The curve run is shown in the figure.*

It was suggested that the tangent distance AE and the angles Δ', Δ'', and Δ''', might be assumed. The angles were taken as they were plotted on the survey map as was also the tangent distance. After the calculations were made the curve was run in the field and failed to close by about four feet. The curve was then laboriously recalculated and rerun twice, checking each time with the first. After the curve had been rerun once another member of the party and myself declared that the mistake lay in assuming the tangent distance; but after much discussion the curve was run a third time and again failing to close, the calculation was put in our hands.

In the following description the following trigonometric formulæ will be referred to by number, the large letters being the three angles of any triangle, A generally being assumed as the largest, and the small letters being the sides opposite these angles.

$$\text{Tan } \tfrac{1}{2}(A - B) = \frac{a - b}{a + b} \tan \tfrac{1}{2}(A + B), \qquad (1)$$

$$a : \sin A :: b : \sin B. \qquad (2)$$

$$\text{Nat. sin } \frac{A}{2} = \sqrt{\frac{(s - b)(s - c)}{cb}}, \qquad (3)$$

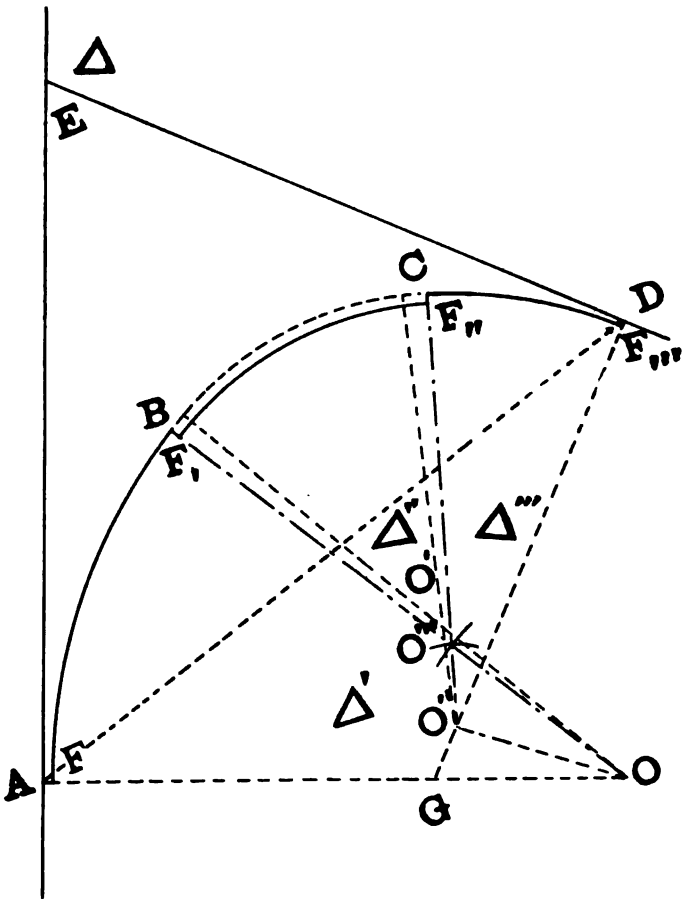
where

$$s = \frac{a + b + c}{2}.$$

* The lettering is to correspond with that in Crandall's "Transition Curve."

The method employed was as follows:
Known: Δ, Δ', Δ'', R', R'', R''', F, $F_{,}$, $F_{,,}$ and $F_{,,,}$.
To find AE and ED.
The third angle is found as

$$\Delta''' = \Delta - (\Delta' + \Delta'').$$



If the curve had no transitions it would be $ABCD$ and the center of the middle curve, O', would lie on the intersection of the radii R' and R''', or their prolongations. With transitions however the distance $F_{,}$ and $F_{,,}$ must be offset inward or outward according to the degree of the various curves employed. So, if, with O as a center and a distance $OO' - F_{,}$ as a radius, an arc is described,

and, with O'' as a center and $O''O' - F_{II}$ as a radius, another arc, intersecting the first, be drawn, their intersection, O''', will be the center of the new curve.

In the triangle $OO'O''$

$$OO' = R' - R'',$$

$$O''O' = R''' - R'',$$

and angle

$$OO'O'' = \Delta''.$$

Using (1) and remembering that $A + B = \Delta''$ the value of the angles $O'OO''$ and $O'O''O$ may be found. The side $O''O$ may then be found by (2).

Then in the triangle $OO''O'''$

$$OO'' = \text{Known from above},$$

$$OO''' = (R' - (R'' + F_I),$$

$$O''O''' = R''' - (R'' + F_{II}).$$

and the angles may be found by (3) $O''O'''O$ being the new Δ''.

$$\text{New } \Delta' = \Delta' - (O'OO'' - O'''OO''),$$

and

$$\text{new } \Delta''' = \Delta - \text{new } (\Delta' - \Delta'').$$

With these the length of the curve, etc., can be computed as usual.

To find the tangent distance. In the triangle $OO''G$.

OO'' is known from above.

$$\text{Angle } OGO'' = 180° - \Delta.$$

$$\text{Angle } O''OG = \Delta' - O'''OO''.$$

$$\text{Angle } GO''O = 180° - (OG - O'' + O''OG).$$

And using (2) GO and GO'' may be found. Then the distance

$$AG = R' + F \pm OG,$$

$$DG = R''' + F_{III} \pm O''G,$$

$$\text{angle } AGD = J.$$

The $\pm$ signs show that the center might so occur that it lay outside AO.

The other angles and AD can be found by using equations (1) and (2).

Then in the triangle AED, AD from above,

$$\text{angle } EAD = 90° - GAD,$$

$$\text{angle } EDA = 90° - GDA,$$

$$\text{angle } AED = 180° - \Delta,$$

and equation (2) will give AE and ED.

This appears to be a very roundabout method but seems to be the only way. The case treated is one of innumerable combinations which may be solved in a similar way which will be suggested by the ingenuity of the engineer.

DESCRIPTION OF A FIRE, LOAD AND WATER TEST.

Made Upon a Reinforced Concrete Floor (Kahn System) at the Fire Testing Station Columbia University.

By IRA H. WOOLSON, E.M.

WEATHER OBSERVATIONS.

Day cloudy to partly fair. Moderate wind from the west. Atmosphere very light, making draft conditions poor. Temperature, 75°–80° F.

Date of Test, Sept. 30, 1904.

Test started 10:30 a. m.

Water applied 2:31 p. m.

Final loading, Oct. 3.

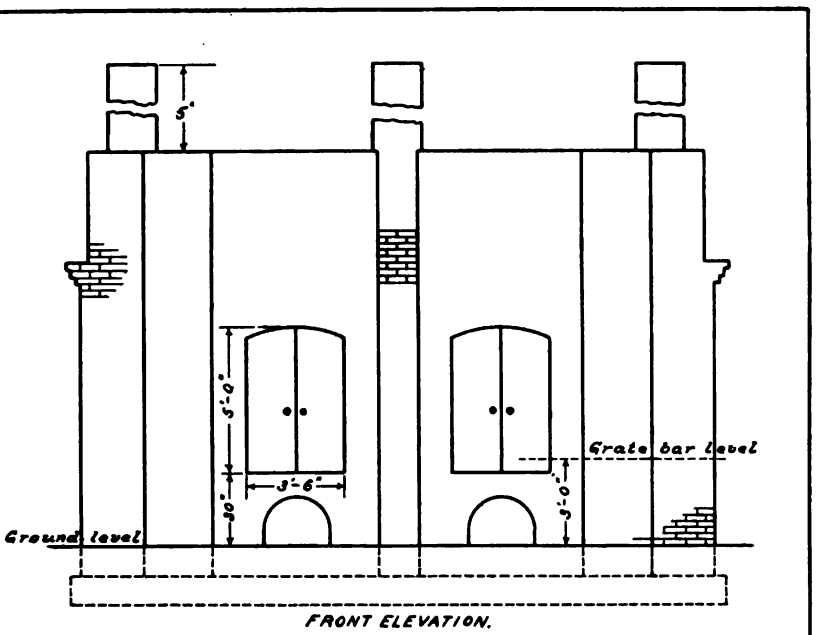
Age of floor when tested, 29 days.

This test was made in strict accordance with the specifications of the New York City Building Bureau, and the installation of the floor as well as the test were at all times under the direct supervision of its Engineering Staff.

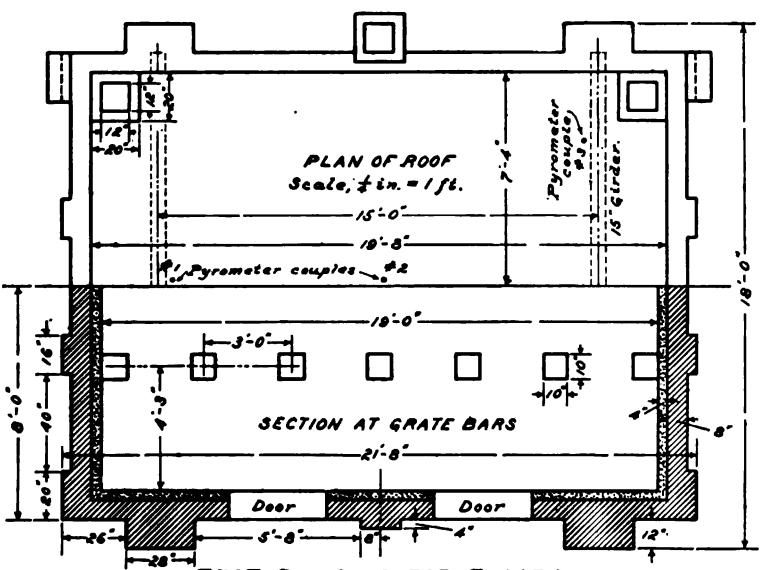
Method of Construction.

The test building is 19′ × 14′ on the inside. The walls are of brick, lined with reinforced cinder concrete. It is supplied with six chimneys and suitable draft openings thru the walls at the bottom. The grate is located 2′ 6″ above the ground. The ceiling is 9′ above the grate. Details of construction are shown in attached sketches.

The floor to be tested constituted the roof of the building, and was carried on two reinforced concrete girders of the same system as the floor. These girders were 18″ deep including the floor of which they formed a part. They were spaced on 15′ centers and had a clear span of 14 feet between the walls. The actual clear span of the floor slab between the girders was 13′ 8″.



FRONT ELEVATION.



TEST BUILDING FOR FLOORS.

FIRE TESTING STATION, COLUMBIA UNIVERSITY.

AMSTERDAM AVE., & 113" ST.,

NEW YORK CITY.

The reinforcing metal in both floor and girders was the peculiar Kahn bar with its wing projections. The bars in the floor were ½″ square. One set spaced on 8″ centers running from girder to girder and another similar set at right angles to the first but spaced 2′ apart. 1″ bars were used in the girders. Full details of the construction of both floor and girders are given in attached drawings.

The concrete for the floor was mixed in proportion of 1 cement, 2½ sand and 5 broken stone, and 1, 2, 4 for the girders. "Vulcanite" Portland cement was used, and the stone was trap rock crushed to ¾″ size.

Ceiling was not plastered.

Purpose of the Test.

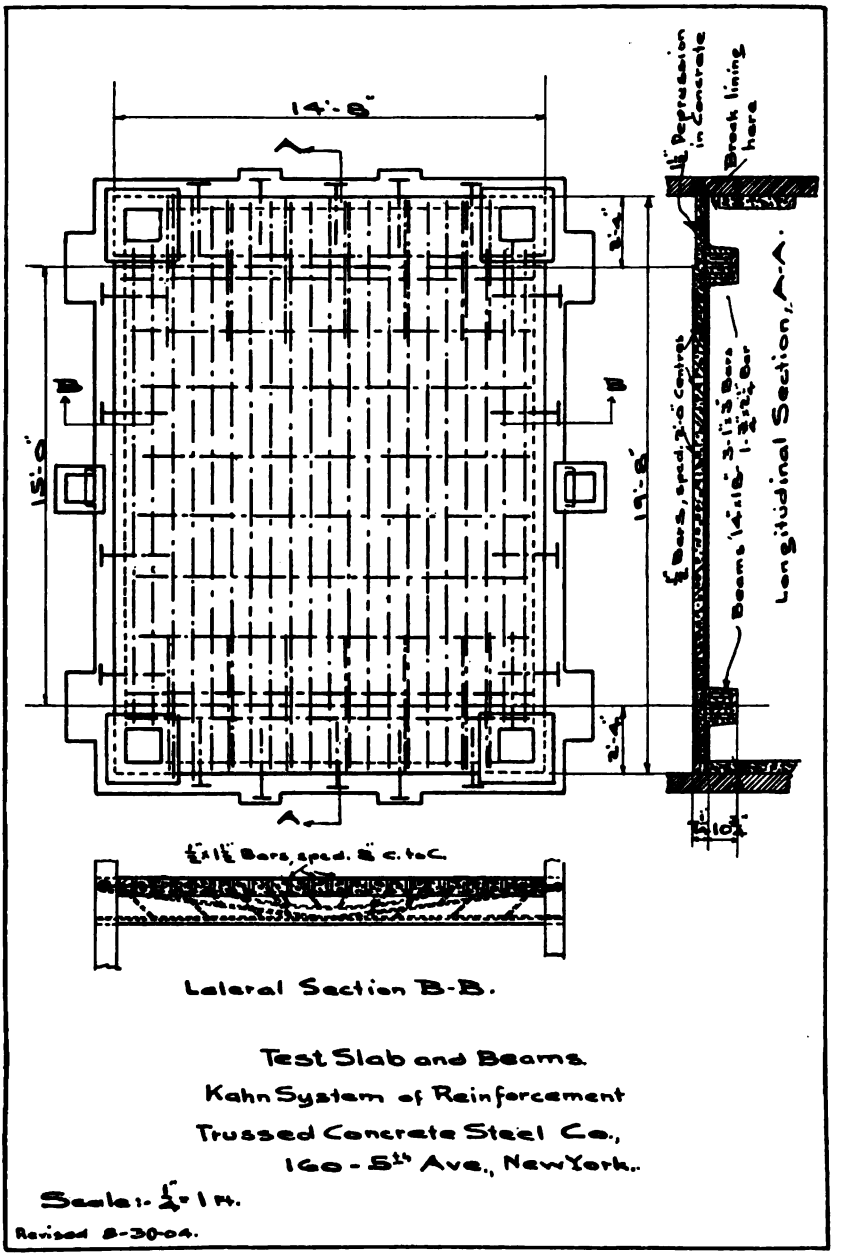
The purpose of the test was to determine the effect of a continuous fire below the floor for four hours at an average temperature of 1700° F., the floor carrying at the same time a distributed load of 150 lbs. per sq. ft.; at the end of the four hours the under side of the floor (or ceiling) while still red hot to be subjected to a 1⅛″ stream of cold water at short range, thru 100′ of hose under 60 lbs. pressure for five minutes, then the upper side of the floor (which forms the roof of the test building) to be flooded at low pressure; afterwards the stream to be again applied at full pressure on the under side for five minutes longer.

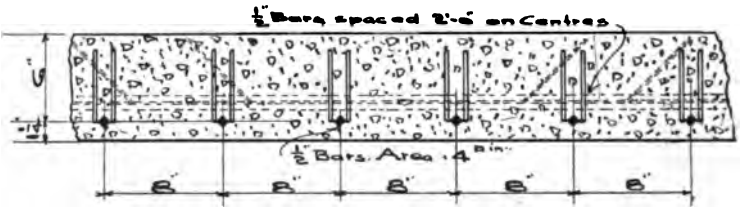
Deflection of beams and floor to be measured continuously during the test. The load then to be removed and when cold reloaded to 600 lbs. per sq. ft. and deflections noted.

Temperatures.

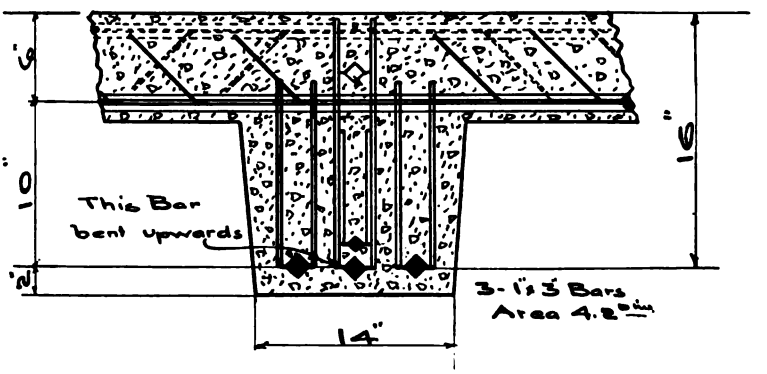
The temperatures of the fire were obtained by electric pyrometer couples suspended thru the floor from above and hanging about 6″ below the ceiling. The location of the couples is indicated on plan of building.

Readings were made upon each couple every three minutes. The fuel used was dry cord wood, the frequency of firing being determined by the temperature of the test chamber. The "Log of Temperature Readings," together with plotted curve for one couple, is herewith attached.


14'-8"
15'-0"
19'-8"
A
B
B
A
Longitudinal Section, A-A.
Break lining here
Lateral Section B-B.
Test Slab and Beams.
Kahn System of Reinforcement
Trussed Concrete Steel Co.,
160 - 5th Ave., New York.
Scale:- 1" = 1 Ft.
Revised 8-30-04.



Cross Section of Floor Slab.



Cross Section through ℄ of Beam.

Details of Test
Floor Slab and Beams,

Trussed Concrete Steel Co,
Kahn System of Reinforcement.
160-5th Ave, N.Y.

Scale 1½"=1'-0"

Revised-8-30-04.

Aug. 19, 1904.

Deflections.

The deflections which occurred at various stages of the test were measured by a Y-level reading upon rods located upon the ends and middle of each girder, also upon the middle and each side of the floor slab. The attached tables give full details of the variations in level thruout the fire and load test.

Water.

The water was applied by firemen with a steamer detailed from the fire engine house at Amsterdam Avenue and 113th Street, under direction of Capt. J. J. Livingston. The pressure gauge was carefully watched and full 60 lbs. maintained.

In applying the water, the stream was thrown back and forth over the whole ceiling as much as possible and not allowed to strike continuously on one spot. After five minutes application the pressure was reduced to about 30 lbs. and the top of the floor flooded 2″ deep, then the stream was applied to the ceiling again at full pressure for five minutes longer.

Effects of the Test.

Owing to the very light atmosphere at the time of starting, the smoke came out of the chimneys and immediately fell to the ground. This condition existed for over an hour, resulting in checking the fire and lowering the temperature. A better atmosphere prevailed during the latter part of the test, and high heat was obtained without difficulty. It was necessary to maintain a rather high temperature during this period to compensate for the low temperature during the early part of the test.

During the test several cracks developed on the roof running in various directions, as the floor sagged from expansion due to the heat. Most of these were $\frac{1}{16}$″ to $\frac{1}{8}$″ in width and 2′ to 4′ long. One started from middle west chimney and ran south parallel to wall and about 1′ from the wall. This opened $\frac{3}{8}$″ on top, but did not appear to extend through to the under side. No cracks were visible on the under side, and later when the roof was flooded no leaking of water thru the cracks was noticeable.

The ceiling was in excellent condition. The concrete was somewhat pitted where subjected to the force of the water, but no flak-

ing had occurred and no cracks were apparent except a horizontal crack about 3 feet long in the side of the south girder, and a few very small cracks in the bottom of each girder.

No exposure of the reinforcing metal was made except a few small holes each about $\frac{1}{2}''$ in area. Practically the metal protection in floor and girders was complete.

By reference to the attached "Data of Deflection Readings" it will be noted there was a deflection of $4\frac{1}{8}''$ in the middle of the floor span during the fire; this included a deflection of $1\frac{3}{8}''$ in the middle of the girders. When the load was removed and the floor allowed to cool the deflection was deduced to $1\frac{5}{8}''$ for the floor, and $\frac{5}{16}''$ and $\frac{6}{16}''$ respectively for the girders. The final loading to 600 pounds per square foot produced a total deflection in the middle of the girders of $1\frac{5}{16}''$ and $1\frac{1}{8}''$ respectively. The deflection of the floor slab relative to the girders when under full load was $2\frac{3}{32}''$.

The full load was left on the floor 16 hours with practically no increase in deflection. After the load was discharged a recovery of about an inch was noted, though it was not accurately measured.

The test was conducted in conjunction with chief engineer Miller and assistant Schwartz of the Building Department, Borough of Manhattan, and the Department was further represented by Messrs. Koen and Schaefer from the Boroughs of Brooklyn and the Bronx respectively.

The Company was represented by Messrs. M. Kahn, R. W. Berliner and S. W. Rothrock. Several architects and members of the Fire Department were also present.

Progress of the test and the condition of the ceiling after test are shown by the following illustrations.

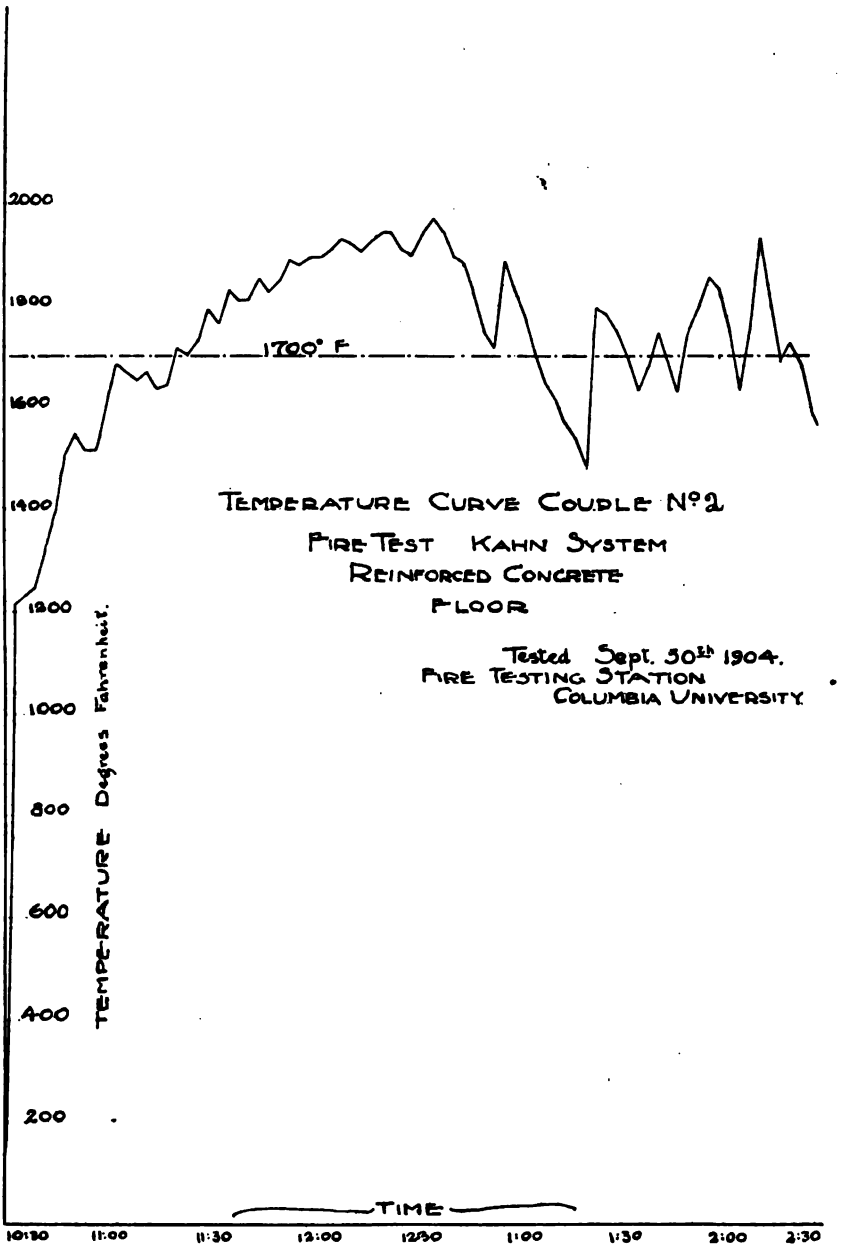
Log of Temperature Readings Taken at Fire Test of Kahn System Reinforced Concrete Floor.

Test started 10.30 A. M., Sept. 30, 1904. Temperatures read by Julian C. Smallwood, Mech. E.

Time.	Couple No. 1.	Couple No. 2.	Couple No. 3.
10.33	967	1216	1321
36	1006	1231	1474
39	1034	1245	1562
42	1110	1321	.....
45	1153	1396	.....
48	1232	1503	.....
51	1307	1548	.....
53	1336	1518	1154
57	1232	1518	1532
11.00	1307	1601	1655
03	1413	1683	1683
06	1390	1669	1676
09	1352	1655	1712
12	1413	1669	1669
15	1367	1638	1683
18	1356	1642	1716
21	1417	1716	1731
24	1432	1702	1731
27	1446	1731	1844
30	1479	1792	1837
33	1502	1765	1644
36	1509	1824	1765
39	1569	1810	1718
42	1502	1810	1839
45	1554	1853	1810
48	1586	1827	1782
51	1664	1849	1768
54	1631	1887	1797
57	1655	1880	1763
12.00	1671	1894	1752
03	1681	1897	1755
06	1703	1912	1778
09	1667	1928	1755
12	1681	1920	1785
15	1732	1904	1785
18	1728	1924	1820
21	1759	1941	1834
24	1775	1941	1789
27	1775	1908	1759
30	1782	1901	1743
33	1792	1944	1882
36	1823	1972	1897
39	1837	1944	1823
42	1837	1897	1792
45	1792	1882	1762
48	1763	1824	1718
51	1725	1747	1675
54	1789	1718	1642
57	1747	1883	1740
1.00	1718	1824	1718
03	1689	1779	1675
06	1642	1703	1613
09	1597	1642	1552

Time.	Couple No. 1.	Couple No. 2.	Couple No. 3.
1.12	1538	1613	1538
15	1538	1568	1509
18	1518	1540	1480
21	1480	1504	1450
24	1691	1795	1795
27	1691	1781	1677
30	1660	1742	1644
33	1616	1692	1600
36	1571	1631	1555
39	1600	1678	1555
42	1631	1743	1600
45	1593	1692	1616
48	1555	1631	1571
51	1631	1743	1586
54	1638	1796	1616
57	1706	1856	1706
2.00	1721	1834	1706
03	1643	1748	1636
06	1546	1636	1560
09	1763	1748	1605
12	1801	1936	1763
15	1711	1801	1711
18	1652	1692	1623
21	1593	1721	1652
24	1586	1685	1638
27	1533	1593	1578
29	1472	1562	1526
Average.	1566.3	1728.6	1676.3

Average of No. 2 and No. 3 = 1702.5°.


2000
1800
1700° F
1600
1400
1200
1000
800
600
400
200
TEMPERATURE Degrees Fahrenheit.
TEMPERATURE CURVE COUPLE Nº2
FIRE TEST KAHN SYSTEM
REINFORCED CONCRETE
FLOOR
Tested Sept. 30th 1904.
FIRE TESTING STATION
COLUMBIA UNIVERSITY
TIME
10:30
11:00
11:30
12:00
12:30
1:00
1:30
2:00
2:30

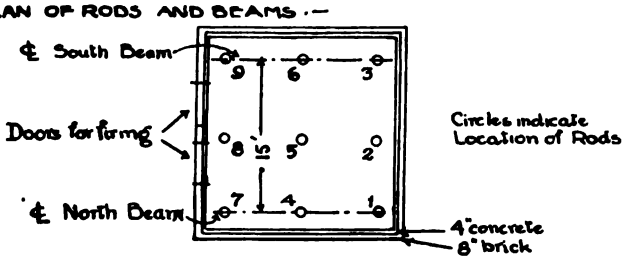
DATA OF DEFLECTION READINGS AT FIRE TEST ON A KAHN SYSTEM REINFORCED CONCRETE FLOOR

made by the

TRUSSED CONCRETE STEEL CO.

Test made at Columbia University Fire Testing Station, Sept. 30, '04
Under the supervision of I. H. Woolson, E.M.

PLAN OF RODS AND BEAMS :—



DEFLECTION READINGS:—

Note. All deflections were downward.
All fractions of an inch denoted below are in sixteenths

TIME	South Beam			North Beam			Middle Span			REMARKS
Sept. 30th	3	6	9	1	4	7	2	5	8	
10:30	0	0	0	0	0	0	0	0	0	Fire Started
10:45	1/	3/	1/	1/	4/	1/	5/	13/	5/	With Load of
11:00	2/	6/	1/	2/	6/	2/	9/	1-4/	9/	150 lbs. per sq. ft.
11:15	2/	6/	3/	2/	7/	2/	9/	1-6/	9/	during Fire.
11:30	3/	7/	3/	3/	8/	2/	12/	1-12/	9/	
11:45	3/	8/	3/	3/	9/	2/	14/	2-1/	15/	
12:00	3/	8/	3/	3/	11/	3/	1-0/	2-6/	1-0/	
12:15	4/	10/	3/	4/	12/	3/	1-0/	2-9/	1-3/	
12:30	4/	11/	4/	4/	14/	3/	1-2/	2-14/	1-5/	
12:45	5/	12/	4/	5/	1-0/	3/	1-4/	3-3/	1-7/	
1:00	6/	14/	5/	6/	1-1/	3/	1-6/	3-5/	1-7/	
1:15	6/	1-9/	5/	6/	1-3/	3/	1-6/	3-8/	1-8/	
1:30	6/	1-3/	5/	6/	1-3/	3/	1-6/	3-10/	1-9/	
1:45	6/	1-4/	5/	6/	1-4/	4/	1-8/	3-13/	1-9/	
2:00	6/	1-3/	6/	6/	1-4/	4/	1-9/	3-14/	1-11/	
2:15	7/	1-5/	6/	7/	1-5/	4/	1-11/	4-1/	1-12/	
2:30	7/	1-6/	7/	7/	1-5/	4/	1-13/	4-3/	1-12/	Water applied at 2:31
DEFLECTIONS DURING FINAL LOADING:—										
	0	5/	1/	3/	6/	2/	3/	1-10/	1/	No load.
Oct. 3	4/	11/	8/	8/	13/	4/	5/	2-3/	1-4/	400 lbs. per sq. ft
	6/	13/	10/	10/	1-3/	5/	9/	3-2/	1-8/	600 " " " "
	6/	10/	9/	7/	12/	5/	7/	1-8/	13/	Effect of total load.

Middle deflection of floor under 600 lbs. load, minus middle deflection of girders = $2\frac{3}{32}$ in.

DEFLECTIONS READ BY
H. L. MEAD

BUILDING BEFORE TEST. LOAD OF 150 LBS. OF PIG IRON PER SQUARE FOOT IN PLACE.

BUILDING DURING TEST.

APPLYING THE WATER AT END OF FOUR HOURS. STAND FOR READING LEVELS AT THE RIGHT.

LOAD OF 600 LBS. PER SQUARE FOOT AFTER THE FIRE TEST.

PORTION OF CEILING AND ONE GIRDER AFTER FIRE TEST.

BOOK REVIEWS.

The Sampling and Estimation of Ore in a Mine. By T. A. RICKARD. The Engineering and Mining Journal, New York, 1904, 222 pp., 35 ills.

As indicated in the preface, the aim of the author has been chiefly to bring together in convenient form many of the contributions to the discussion of this important subject which appeared in the *Engineering and Mining Journal* during the year 1903. These contributions are preceded by an introductory article of 75 pages by the author, on the more important parts of the work underlying a mine report — as it should be; dealing with the determination of average value of the ore, the actual operation of taking the samples, size of samples, mode of calculating values as based on the sampling, inferences from sampling and precautions as to the weight to be allowed for abnormally "high assays," possible discrepancies between the values resulting from sampling and those from actual mining, estimation of ore-reserves and the future prospects of a mine

The author emphasizes and deals critically with the various phases of these operations and determinations which formed the substance of the late discussion and which aroused so much interest in the profession. Instead of attempting a lengthy treatment of the subject, he has preferred to point out some of the pitfalls into which the unwary may be led and has then appended in full the most notable contributions referred to above, each under the name of its author.

In some respects the result may be considered at present as more satisfactory than if the mass of material had been worked up into a compacter form. It is evident that the subject is far from being exhausted and it still remains for some benefactor of his fellow engineers to attempt a fuller exposition.

In encouraging this discussion, the author has rendered a service which will be appreciated by every mining engineer, and it is not too much to say that it has resulted in a better understanding in the profession of certain terms and phrases which have often been loosely and even dangerously applied. "Ore blocked out," "ore developed," "ore in sight," are expressions which were greatly in need of definition. One of them — "ore in sight" — is now so discredited that few will have the hardihood to continue its use seriously. Perhaps it is unreasonable to expect that its place will be supplied by any term sufficiently concise and accurate to be generally accepted. Though the phrases "ore blocked out" or "ore developed" are distinct improvements, yet even these demand explanation and limitation wherever they are employed. Notwithstanding all that has been written and said, probably no two engineers would agree upon their exact meaning and scope, nor is it to be expected that they should. No two mines are alike and mining is not an exact science. It is impossible to attain uniformity in dealing with work carried on under an infinite variety of conditions.

In closing, the author comments briefly upon the points brought out by the several contributors to the discussion. The following quotation (p.

205) will indicate his position with regard to some of the common features of mine reports: "It is the net profit that an engineer is asked to determine; all the rest is noise and smoke; tonnage of ore, assays, machinery, water power, timber rights, dump facilities, scenery — all these are mere frills on the outside of the essential problem. How much money will the mine yield? This is being recognized more and more; twenty years ago it was customary to make a perfunctory trip through the underground workings, to break off a specimen or two and then to spend a few days copying the past records of production, getting tracings of the maps and interviewing the oldest inhabitants. With such data, it is no wonder that mine reports became a thing for derision."

There has been, and doubtless still is, in many cases, substantial ground for this caustic criticism. While many of the matters referred to are legitimate subjects for investigation, and must be carefully weighed and considered in arriving at an intelligent opinion on a mine, it is unnecessary that they should appear in the report in extenso, filling page after page and obscuring the essential features of what should be a plain, common-sense, commercial document. If they *must* have their place, the report should at least close with a concise and definite statement of the engineer's opinion as to the financial aspects and future prospects of the property. R. P.

Geology Applied to Mining. A concise summary of the chief geological principles, a knowledge of which is necessary to the understanding and proper exploitation of ore-deposits. For Mining Men and Students. By Josiah Edward Spurr, A.M., Geologist, U. S. G. Survey, etc., etc. New York: Engineering and Mining Journal, 1904, pp. 326, 70 cuts.

A number of books have been written on the Genesis and Geology of Ore-Deposits, and the technical literature of the past ten years contains a mass of material bearing on the subject. Some of the latter has been addressed by geologists chiefly to geologists, but much of it, also, has a direct and important bearing on the field of work and the professional education of mining men.

To assert that the principles influencing the formation of ore-deposits and the frequent association of certain ores with certain geological formations are better understood now than formerly is a platitude. Not long ago it was a common saying that the miner could see no farther below the earths' surface than the bottom of a drill-hole or of a shaft. But a mining man who will study carefully the valuable recent literature on the subject, and who by its aid will endeavor to interpret the phenomena which he observes in the field, has it in his power now to see farther than this and to perceive more clearly the nature of the often complex processes influencing and controlling ore-deposition.

In writing the present volume Mr. Spurr has endeavored to present "concisely the results of the Science of Geology which bears upon ore-deposits." He addresses himself to "those who have had little to do with geology as a science," or with the theory of ore-deposits. The ground covered includes: Processes of Ore-Concentration from the Surrounding Rocks, and Studies of the Stratified and Igneous Rocks, together with a discussion of Dynamic, Structural and Chemical Geology as applied to Mining.

Most of the features of the book which might be considered open to criticism have been anticipated by the author himself in the preface, and the most unfriendly critic would find little left to say. It might possibly be thought an unwise admission, however, when the author states candidly that the work was published before it had been so far perfected in form and substance as to meet with his own entire approval.

Throughout the book there is an evident endeavor to make clear statements without using too many of those geological terms and turns of expression, which, while familiar as to their derivation and precise application to professional geologists, may be understood imperfectly by mining men in general. To accomplish this aim satisfactorily would unquestionably be difficult in treating of any technical subject, but the author seems to have succeeded remarkably well. In presenting the subject matter the form of question and answer has been adopted. For many of the questions propounded it is hardly possible to frame answers at once concise and comprehensive and the writer of this notice ventures to express the opinion that some system of paragraphing would have been preferable. To give the desired prominence to subdivisions of the text the paragraphs could be headed by heavy-faced type. But, after reading the book one is much more inclined to approve than to find fault. It is compact — though of an unnecessarily high specific gravity —, is so arranged that any given topic may readily be found and will certainly be found useful, specially by those actually engaged in field work.

R. P.

A Systematic Handbook of Volumetric Analysis. By FRANCIS SUTTON. Ninth edition. Philadelphia, Blakiston's Son & Co. 1904. 8vo, pp. 617.

In reviewing a new edition of such a well-known book as "Sutton's Volumetric Analysis" it is most important to point out the changes from the preceding edition.

As the author states in the preface, the new material added has been taken very largely from abstracts which have appeared in certain important journals. This material is in the main an improvement to the work, but the additions are not characterized either by completeness or by especial care in their selection; they seem to be those which have happened to come to the notice of the author rather than those which might have been selected after a thorough examination of the entire field.

The work is, as it has been in the past, the most useful collection of practical volumetric methods in the English language and should be in the library of every chemist. No attempt is made at a scientific treatment of the subject. No position is taken on disputed points. This is made evident by an extract from page xi: "The formulæ are constructed on the basis of $H = 1.0 = 16$ $H_2O = 18$." It seems almost incredible that any chemist in the twentieth century can thus calmly ignore the fact that the ratio of oxygen to hydrogen is not 16 to 1, and give a table of atomic weights which do not agree with either of the standards which have been the subject of so much controversy during recent years. As these values affect the strength of nearly all the solutions used, though of course to a very slight extent, attention is called to this fact.

The book has been entirely reset so that the added material has not increased the size of the volume.

E. H. M.

ALUMNI NOTES.

DEPARTMENT OF GEOLOGY.

The field session with the mining engineers and graduate students was held this year in the East on account of the large size of the prospective class. Professor Kemp did not feel that he alone could efficiently care for forty to fifty in a western locality. The vicinity of Rondout on the Hudson was selected and a party of 104 was mustered there on May 29. The party was divided into 9 or 10 squads, each with a captain. Professor Kemp, Professor Grabau, Dr. Berkey, Dr. Campbell, Professor Marsters, of Indiana University, and from our graduate students, Messrs. Swartz, Wilson, Goldman and Kirk, each had charge of a party. The locality is singularly well adapted for instruction in structural geology. Ten contrasted formations can be seen, most of which have their own index fossils, while faults, folds and unconformities are displayed with wonderful clearness in the cement quarries. Through the kindness of Mr. Edward Coykendall, C. E., '95 and Mr. Clarke of the Cement Company, the success of the work was greatly facilitated. The week before the field session at Kingston, the graduate students of the department, nine in number, made a week's trip into the Helderberg mountains with Professor Grabau. Indian Ladder, Countryman's Hill, Mt. Becraft and Mt. Merino were visited and the stratigraphy studied.

During the summer Professor Kemp completed the maps and manuscript of that portion of a folio of the U. S. Geological Survey which had been assigned to him. It embraces the mountainous region between Lake George and Lake Champlain. Professor T. N. Dale has the eastern portion of the area in charge and the final result will be a joint production. Professor Kemp served for two weeks in September upon the International Jury of Awards in Mining and Metallurgy at St. Louis.

Professor Grabau gave courses in the Summer Session, being assisted by Dr. Maury. Paleontology was offered for the first time. The attendance was about the same as in the previous year. At the close of the session a three days' trip was taken, the localities visited being Rosendale, Rondout, and Mt. Becraft.

The month preceding the Summer School was spent by Professor Grabau in completing the field work for the Geological Bulletin of the Schoharie region, now in course of publication by the New York State Survey. After the Summer School some time was passed in the Utica region where Professor Grabau studied the problems of overlap in Siluric strata.

Dr. Berkey passed the summer in Minnesota doing some field work upon problems begun in former years.

Dr. Julien has also been completing several papers which have been in progress for some years past.

Dr. Ogilvie has received a year's leave of absence from Barnard and is passing it in the West. As a result of two or three months in the Canadian Rockies a paper has just appeared in the Journal of Geology.

Through the kindness of Mr. Jerome B. Wheeler of Manitou, Colorado, the department has received a large model of the Bonnybel Mine

near Aspen, Colo. This model illustrates the local geology and is a very welcome addition to the Museum.

A number of Cambric fossils from Pioche, Nev., have been presented to the department by Mr. Charles Of. Much new material has also been obtained through collections made by various students and friends.

The department opens the year with a gratifying number of students, especially candidates for advanced degrees. Besides six working for Ph.D. there are ten to fifteen looking forward to A.M. Field work was carried on by a number of these students, Mr. Goldman in the Black River region, Mr. Wilson on Nantucket Island, Mr. Prather at Atlantic Highlands, Mr. Bateson in southern California, and Mr. Marsters in Vermont.

J F. K.

ELECTRICAL ENGINEERING DEPARTMENT.

S. M. Day and J. L. Lewinson, graduates in electrical engineering, 1904, have been appointed assistants in the electrical engineering department.

During the summer, improvements have been made in the various laboratories, which include the addition of some motors and dynamos in the direct-current laboratory and the setting up of some street railway motors, with excellent facilities for testing. Some of the standards of the department have been certified at the National Bureau of Standards, thus increasing our facilities for standardization. This is an important feature of the department's work and is being carried out systematically from year to year.

During the sesquicentennial the graduates of the electrical engineering department celebrated the fifteenth anniversary of the founding of the electrical engineering department by holding a subscription dinner on the evening of October 28, 1904, in rooms 301 and 302, Engineering. Professor F. B. Crocker, as chairman of the dinner committee, introduced the speakers.

Professor Sever and Mr. Townsend are about to publish their laboratory note-book, covering the direct, alternating and instrumental laboratory work of the third and fourth years. The title is "Laboratory and Factory Tests in Electrical Engineering." Professor Crocker's text-book on "Electric Lighting," Volume I., has been completely revised.

During the summer Professor Sever was called to St. Louis as a member of the International Jury of Awards in Electricity at the Louisiana Purchase Exposition.

G. F. S.

ORGANIC CHEMISTRY.

Since the last publication of notes from this department the following matters of interest have occurred:

For the first time in the history of our Summer Session, courses were offered this year in Organic Chemistry. Of the two courses offered, Chemistry 20 (Elementary lecture course) attracted 14, and Chemistry 30 (Elementary laboratory course) 6 students. Both were in charge of Dr. H. T. Beans, who took his Ph.D. in Organic Chemistry last year, and is now a tutor in Qualitative Analysis.

Recent publications by officers of the department include the following: "Review of American Chemical Research," by M. T. Bogert, *Jour. Amer. Chem. Soc.*, XXV., R. 559–566; XXVI., R. 7–12, 60–66,

101–106, 163–166, 206–210, 291–292, 346–349, 373–383; "Metaminobenzonitrile and Some of Its Derivatives," by M T. Bogert and H. T. Beans, *Jour. Amer. Chem. Soc.*, XXVI., 464–499; "A Further Investigation of the Action of Phenols and Alcohols on the Chlorides of Paranitroorthosulphobenzoic Acid," by V. J. Chambers, *Am. Chem. Jour.*, XXX., 373–392; "Review of American Chemical Research," by V. J. Chambers, *Jour. Amer. Chem. Soc.*, XXXI., R. 210–212, 245–251, 292–294.

The investigations now under way are as follows: Nitriles, quinazolines, substituted orthophthalic acids, the relation between structure and fluorescence in the fluoresceins, substituted anthranilic acids, ureides and pentadiazenones.

Those conducting these investigations include Mr. R. R. Renshaw, the University Fellow in Chemistry, who comes to us from the Pacific coast; Mr. B. L. Murray, chemist of the well-known drug house of Merck & Co., and Dr. Ralph G. Wright, a former graduate of our School of Chemistry and a Ph.D. of Zürich. Dr. W. F. Hand, Professor of Chemistry at the Mississippi Agricultural College and State Chemist of Mississippi, who received his Ph.D. from Columbia last year, is continuing in his own laboratory, under the direction of Professor Bogert, his investigations in the synthesis of the substituted anthranilic nitriles and substituted quinazolines. Some 40 or 50 compounds entirely new to chemistry, discovered as the result of these investigations, are now at the St. Louis Exposition. Dr. Salant, one of the research workers of the Rockefeller Pathological Institute, is taking an elementary laboratory course (Chemistry 30) as a necessary equipment for his work in pathology.

All the courses in Organic Chemistry show a slightly increased registration as compared with last year's figures.

Dr. Chambers has completed his work for the Century Dictionary and for the Encyclopedia Americana.

The grade of the head of the department has been changed from an adjunct professorship to a full professorship. Professor Bogert has been elected a member of the Board of Editors of the *University Quarterly*, and a Councilor-at-large for the next three years of the American Chemical Society. On the occasion of the recent annual meeting in New York of the Society of Chemical Industry, under the presidency of Sir William Ramsay, Professor Bogert was one of the Vice-Presidents. As one of the committee in charge of the special train of the Society of Chemical Industry, he assisted in escorting through our country the chemists from abroad. In appreciation of his services upon this tour and as a token of personal friendship, he was the recipient of a handsomely engraved gold match box, accompanied by a letter of thanks signed by every foreign member of the party. The presentation was made in Boston at the close of the trip, Sir William Ramsay speaking for the visitors. Professor Bogert was invited to deliver one of the two principal addresses before the Section of Organic Chemistry of the International Congress of Arts and Science at St. Louis, and also to act as Secretary of the Section, but was obliged to decline both invitations on account of the meeting of the Society of Chemical Industry referred to above. During the past year he has delivered several public lectures on topics related to Organic Chemistry.

M. T. B.

Woodbridge School,

FORMERLY

School of Mines Preparatory School.

---

417 Madison Avenue,

Between 48th and 49th Streets, NEW YORK CITY

Twenty-fourth Year Begins October 1st, 1905.

THE school is well equipped with physical and chemical laboratories, in which the students are required to perform a complete set of experiments illustrative of their recitations in physics and general chemistry. A special laboratory is devoted to qualitative chemical analysis for advanced students.

Five hundred Students of Columbia School of Mines have been instructed in the Woodbridge School. Also a large number have been prepared for Massachusetts Institute of Technology, Stevens Institute, Sheffield Scientific School, Lawrence Scientific School, Troy Polytechnic Institute, Cornell University, and the Classical, Medical, and Law Departments of Harvard, Yale, Columbia and Princeton.

A summer school for students who have failed in June begins August 13th and coaches men for the Fall examinations. All classes are limited to five. College men are coached in Freshman and Sophomore Mathematics and Quantitative Analysis.

An advanced course for older students prepares them to enter the second year class. Last June one of our students received his degree in Electrical Engineering in three years.

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THE

SCHOOL OF MINES QUARTERLY.

A

JOURNAL OF APPLIED SCIENCE.

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THE LABORATORY FOR THE TESTING OF ROAD MATERIALS AT COLUMBIA UNIVERSITY.

BY A. BLACK, C.E.

The laboratory for the testing of the materials employed in road construction was installed in the Department of Civil Engineering of Columbia University during the winter of 1899–1900, and it has been in practically continuous operation since that time.

The methods of testing such materials in the United States have developed from the earlier tentative experiments inaugurated by the Massachusetts Highway Commission in 1893, and carried on with the collaboration of the U. S. Geological Survey, in the laboratory of the Lawrence Scientific School of Harvard University.

From the beginning of the work, changes and modifications have been introduced as experience dictated, both in appliances and in procedure, resulting finally in the establishment of the present forms of apparatus and methods of testing, which are closely followed in the several road engineering laboratories that have come into existence within the last three or four years.

At a recent meeting of the American Society for Testing Materials, standard methods were adopted for the Abrasion Test; and at the present time a sub-committee of the Society is laboring with the problem of simplifying and standardizing the Cementation Test.

The qualities required in a good road stone are *hardness*, which, in this connection, may be defined as the resistance offered by a material to the displacement of its particles by friction; *toughness*,

or the quality which will enable it to endure light but rapid blows without breaking or spalling; and, for broken stone roads, *binding* or *cementing properties* of the finer abraded material; also, to a less extent, the ability to resist the disintegrating action of the weather, and, probably, of some organic acids produced by the decomposition of excretal matters always present upon roadways in use. These qualities are seldom found together in the same stone. Igneous and siliceous rock, although frequently hard and tough, do not consolidate so well, nor so quickly, under the traffic as limestone, owing to the fact that the sandy detritus formed by such rocks has no cohesion; while the limestone yields a fine material which acts like mortar in binding the individual stones together. A stone with good binding properties will frequently wear much better than a harder and tougher material deficient in such properties. The engineer, therefore, is often called upon, in selecting a road material, to make a judicious compromise between the different requisite characteristic properties of a first-class roadway, to suit the particular conditions and the special problems presented; and it is the object of the testing laboratories to furnish him with the necessary data for this purpose.

Resistance to Abrasion. — The apparatus used for this test is essentially the old Deval machine used in France since 1878, or earlier. In its original form it consisted of two iron cylinders, each 20 centimeters in diameter, and 34 centimeters long, interior measurements. Each cylinder was closed on one end, and had a specially fitted cover on the other, which, by means of a leather gasket, could be bolted on air-tight. The cylinders were attached to a horizontal shaft, to which they were inclined at an angle of 30 degrees, and about which they were rotated by means of a pulley wheel fastened to the shaft.

FIG. 1.

In the Laboratory of the Department of Civil Engineering, the abrasion machine is essentially that described above, except that

there are four cylinders on the same shaft, so that it is possible to make four abrasion tests simultaneously. A counter is used for recording the number of revolutions. Fig. 1.

In the Laboratory of the National School of Roads and Bridges in France, in order to increase the output of the machine, the number of cylinders has been increased to eight, and they are mounted in two rows, on parallel shafts geared to rotate with the same speed.

The material to be tested is broken into pieces from one and one-fourth to two and one-half inches in diameter, the sizes usually employed on road-ways, and as nearly cubical as is practicable with the appliances ordinarily used for such work. These stones should be thoroughly washed, and, if necessary, scrubbed, to remove all dust and foreign matter; and should then be allowed to dry for several days before being used. Five kilograms of the clean broken stone, accurately weighed, constitute the charge for each cylinder. The cylinders being charged, the covers are bolted on securely, and the shaft rotated at the rate of 2000 revolutions per hour, for five hours. Each rotation throws the pieces of stone twice from one end of the cylinder to the other, causing them to grind against one another and against the sides and ends of the cylinders.

Formerly, metal balls, or cubes, were placed with the charges in the cylinders to hasten the wear, and to more nearly reproduce the additional effect of the impact of the horses' hoofs on the road-way; other experimenters mounted the cylinders at right angles to the shaft; but these, and other modifications, are no longer recognized as standard.

When the counter has recorded 10,000 revolutions, the machine is stopped, the covers unbolted, and the contents carefully scraped and brushed out of the cylinders into the upper of two superimposed sieves, having 16 and 100 meshes to the linear inch respectively. These sieves rest on the edge of a broad pan which receives all that passes through them.

The material retained on the upper, or coarser, sieve is thoroughly washed, and then put aside to dry for about two days. It is then carefully weighed, its weight deducted from the original cylinder charge, and the difference recorded as *loss due to abrasion*; for it has been agreed to consider as *abraded* all that passes the sieve with 16 meshes to the linear inch; while the larger

particles retained on that sieve are assumed to be the original pieces reduced by wear, or broken into smaller pieces by impact.

This simple method, by differences, of determining the abrasion loss, should always be used in preference to the laborious and not more accurate method, sometimes prescribed, of weighing directly the finer material, which involves the thorough washing of the cylinder to remove the adhering dust, and the washing of the larger particles in the same water, which must then be filtered, the filtrate, when dry, mixed with the cylinder detritus previously set aside, and the mixture sifted on the 16-mesh sieve, the material passing through this sieve being then weighed.

In the Road material Laboratory of the U. S. Department of Agriculture, the 5 kilogram charge of stone, after being thoroughly cleansed, is dried in a hot-air bath at 100 degrees C., and then cooled in a desiccator. After the test, the fragments retained on the 16 mesh sieve are again thoroughly washed, dried in the hot-air bath at 100 degrees C., and cooled in the desiccator before weighing.

The numerical value for the abrasion of the specimen may then be stated in either of two ways: by the percentage, by weight, of the original charge that has been worn off by abrasion; or the French coefficient of wear may be used, which has been developed from the following considerations :—

In the earlier French tests, a rock of superior wearing qualities was always placed in one of the cylinders as a standard of comparison; and the ratio of the weights abraded, in the case of the standard rock and of the specimen under test, was supposed to indicate their relative resistances to abrasion. It was soon found that only the best varieties of rock produced less than 20 grams of abraded material per kilogram of original charge; the number 20 was, therefore, adopted as a "standard of excellence," and the coefficient of wear for any stone tested was obtained from the formula:—

$$\text{Coefficient of wear} = \frac{20 \times 20}{w} = \frac{400}{w}$$

in which w represents the weight in grams abraded per kilogram of original charge. Table I exhibits maximum and minimum values for abrasion in the case of various classes of materials.

TABLE I.

ABRASION TEST.

Name of Material.	Number of Samples.	Per cent. of Wear.		Coefficient of Wear.	
		Maximum.	Minimum.	Maximum.	Minimum.
Amphibolite	6	4.6	1.5	26.7	8.5
Andesite	3	6.4	2.6	15.2	6.3
Basalt	6	16.6	1.7	23.6	2.4
Chert	10	27.9	2.7	14.6	1.4
Clay	1	19.1	19.1	2.1	2.1
Conglomerate	2	12.7	5.7	7.0	8.2
Diabase	14	6.3	1.2	34.5	6 4
Diorite	8	3.4	1.9	20.6	11.7
Dolomite	15	18.6	2.5	16.1	2.2
Eclogite	1	2.9	2.9	13.8	13.8
Felsite	2	3.4	1.9	21.3	11.9
Field stone (erratics)	1	5.0	5.0	8.0	8.0
Flint	1	7.2	7.2	5.5	5.5
Gabbro	1	2.9	2.9	14.3	14.3
Gneiss	6	5.2	1.9	20.7	7.7
Granite	15	14.8	1.8	21.7	2.7
Limestone	46	34.2	2.8	14.2	1.2
Mixed stone	1	8.7	8.7	4.6	4.6
Peridotite	1	3.6	3.6	11.1	11.1
Quartzite	3	3.6	2 2	18.2	11.1
Rhyolite	9	9.7	1.8	22.9	4.1
Sandstone	7	31.8	3.4	11.6	1.3
Schist	16	7.1	1.9	20.6	5.7
Shale	2	16.2	4.7	8.6	2.5
Slag	2	8.3	7.6	5.2	4.8
Slate	2	6.9	4.7	8.5	5.3
Syenite	1	2.8	2 8	14.4	14.4

For a time the Road Material Laboratory of the U. S. Department of Agriculture employed a new coefficient, called the *department coefficient*, and designated it, for the sake of distinction, U. S. A. D. It was obtained by subtracting 4,000 from the weight, in grams, of the abraded material larger than 3 centimeters, and dividing the difference by 10. "This term was introduced to secure a result with more range to it, and one that could be more easily understood by the average layman."

The abrasion test consumes five hours of time. In order to determine whether it would be practicable to reduce the time, and obtain results comparable with the values secured in the ordinary way, the Road Testing Laboratory of the Maryland Geological Survey undertook some experiments for the purpose of determining the relation between the amount of dust worn from a given sample of stone and the number of revolutions of the cylinder. Two stones of uniform texture were selected for this purpose, a hard

diabase and a medium-grade limestone. The method first tried was to stop the machine several times in the course of a complete test, take out the stones, clean and weigh them. They were then returned to the cylinder, and the revolutions continued. After the 10,000 revolutions had been made, it was found that the stones had suffered materially more abrasion than if they had not been cleaned during the course of the test. This was due to the removal of the dust which, under the ordinary conditions of the test, clings to the stones and affords some protection from wear. The method was then changed, and the experiment carried on as follows: A charge of stone was put in the cylinder, rotated 250 times, removed, and the abrasion determined. A fresh charge, but quite similar to the first, was subjected to 500 revolutions; a third to 1,200; a fourth to 2,000; a fifth to 3,000; a sixth to 5,000; and a seventh to 10,000. From to 20 27 tests were made with each of

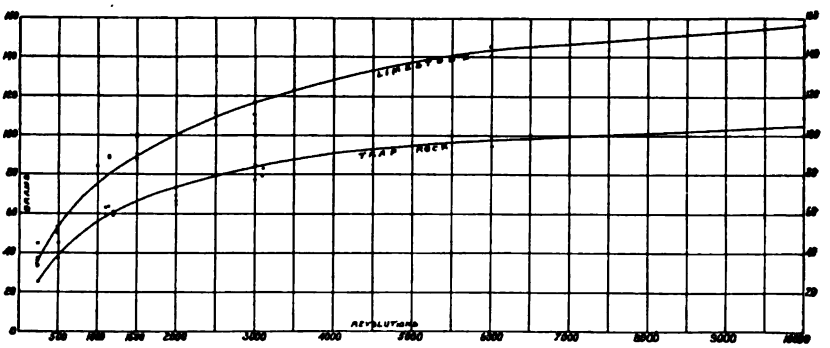


FIG. 2.

the two kinds of stone, the results plotted, and the smooth curves drawn through the points thus obtained as indicated in Fig. 2, which shows that the rate of wear is greatest in the early part of the test, before the stones have been worn smooth, and is undoubtedly due to the greater ease with which the edges and corners are broken off, and to the small quantity of dust protecting the stone from sharp blows. A comparison of the two curves shows that the *relative* amounts worn off from the stones is nearly the same for an equal number of revolutions, whatever that number may be. It is possible, therefore, to determine the coefficient of wear with fewer revolutions than 10,000; for example, if the amount of dust formed by a certain sample in 6,000 revolutions is 129 grams, or *nine-tenths* of that formed by the limestone, then it

would form *nine-tenths* as much dust as the limestone in 10 000 revolutions, and its coefficient of wear would be *ten-ninths* that of the limestone. It is not well to use too small a number of revolutions for this test, for the first part of each curve rises quite rapidly; and the various tests show large variations; but from four or five thousand revolutions onward the curves do not change rapidly, and tests made with other stones, but not plotted on this diagram, shows a greater uniformity in this part of the curves.

A series of tests was undertaken to determine how the result of the abrasion test would be affected by *varying sizes* of the individual stones in the original 5 kilogram charge; and also another series, using *less than 5 kilograms* for a charge, but keeping the average size of the individual stones about the same. The samples were from the same rocks that had been employed in the preceding experiment, and many tests were made with each. The results, however, proved to be too indefinite, and even contradictory, to admit of the formulation of even an approximate general law.

When the value of the resistance to wear by rubbing is required, the Dorrey machine is employed. The standard method of the French School of Roads and Bridges is as follows:

The specimens to be tested are cut into rectangular prisms, 4 centimeters by 6 centimeters base, and 8 centimeters high. They are tested in sets of two, and are held in clamps against the upper surface of a circular grinding disc of cast-iron, on opposite sides of, and 26 centimeters from, the center. The specimens are weighted to press against the grinding disc with a pressure of 250 grams per square centimeter. Sand, obtained by crushing quartzite and screening to standard size, is fed onto the disc through a funnel, allowing one liter of sand, per specimen, for each thousand turns. The disc is rotated at the rate of 2,000 revolutions per hour, for two hours, or 4,000 revolutions for a test.

After 2,000 revolutions the specimens are reversed, to take into account a possible difference in texture in the two parts. The diminution in height is measured, and the loss in weight determined, after each 1,000 turns of the disc. Tests should be made on at least three samples of each specimen, and their average taken as the final result. Usually the loss in height after 4,000 revolutions is used in comparing different road stones; and frequently a specimen of some standard rock, as Yvette sandstone, is placed on the disc and tested with the other specimens, and the reduction in height referred to that of the standard.

This method has not come into general use in road material laboratories in the United States.

The Cementation Test. — The purpose of the cementation test is to obtain the relative binding powers of the various stones used in road making. Good binding power has long been known to road builders to be one of the most important properties possessed by a satisfactory road stone. If the fine material of a road binds well, it protects the coarser stones beneath from wear, withstands better the action of wind and rain, and prevents water from getting to the foundation of the road. Cementing power is thus seen to be a very important and valuable property of any road material. Experiments had been carried on for some five years, in the laboratory of the Massachusetts Highway Commission, to determine some way of testing this important property. The test finally adopted was an impact test, to which stone dust briquettes are subjected. The method in quite general use until recently is as follows:

To make a briquette, dust that is to be tested is passed through a screen with 100 meshes to the linear inch, and is obtained either from the detritus of the abrasion test, or by specially reducing the stone. The reduction can be accomplished by placing some fragments of the stone in one of the cylinders of the abrasion machine together with one or more steel weights, and allowing the machine to run until a sufficient quantity of the stone is pulverized. The dust is made into briquettes of circular section, 25 millimeters in diameter and 25 millimeters in height, by placing, in a metal die of proper dimensions, the dust mixed with only enough distilled water to moisten it (about 4 cubic centimeters), inserting a closely fitting plug on top of the wet dust, and subjecting it to a pressure of 100 kilograms per square centimeter. The necessary weight of dust varies with the density and compressibility of the material, but generally it requires about 25 grammes of dust to make a briquette of the above dimensions. Two weeks are usually allowed for the briquettes to dry, at the ordinary temperature of a room.

Cuts of the machine for testing these briquettes are shown in Figs. 3 and 4. It consists of a 1 kilogram hammer (*H*), arranged like the hammer of a pile driver, on two vertical guides (*D*). The hammer is raised by a screw (*C*), and dropped automatically from any desired height. It falls on a plunger (*B*), which rests upon the briquette (*O*) to be tested. The plunger (*B*) is bolted to

a crosshead (G), which is guided by two vertical rods (F). A small lever (J), carrying a pencil (K) at its free end, is connected to the side of the cross head by a link motion, arranged so that it gives a vertical movement to the pencil six times as great as the

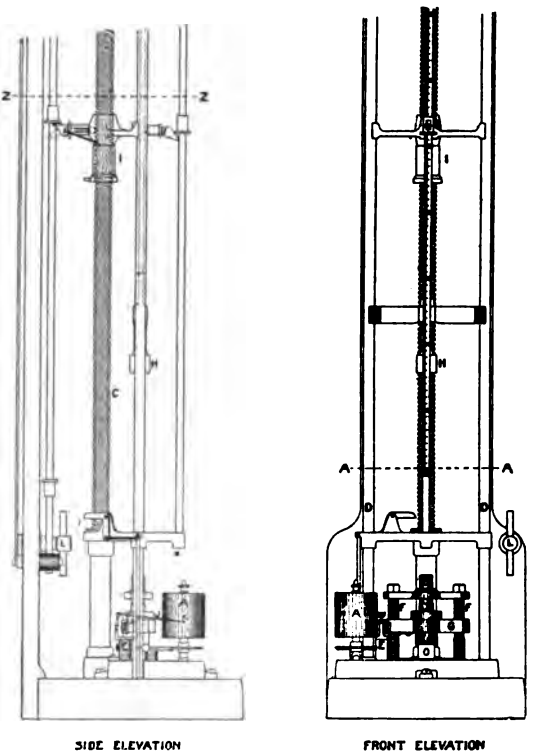


FIG. 3.

movement of the cross head. The pencil is pressed against a drum (A), and its movement is recorded on a slip of paper fastened thereon. The drum is moved automatically through a small angle at each stroke of the hammer; in this way a record is obtained of the movement of the hammer after each blow. The standard fall of the hammer for a test is 1 centimeter, and the blow is repeated until the bond of cementation of the material is destroyed. The final blow is easily ascertained; for, when the hammer falls on the plunger, if the material beneath it can withstand the blow, the plunger rebounds; if not, the plunger stays at the point to which it is driven, the elasticity of the material being completely destroyed. The automatic record thus obtained from each

briquette is filed for future reference. The *number of blows* required to break the bond of cementation, as described above, is

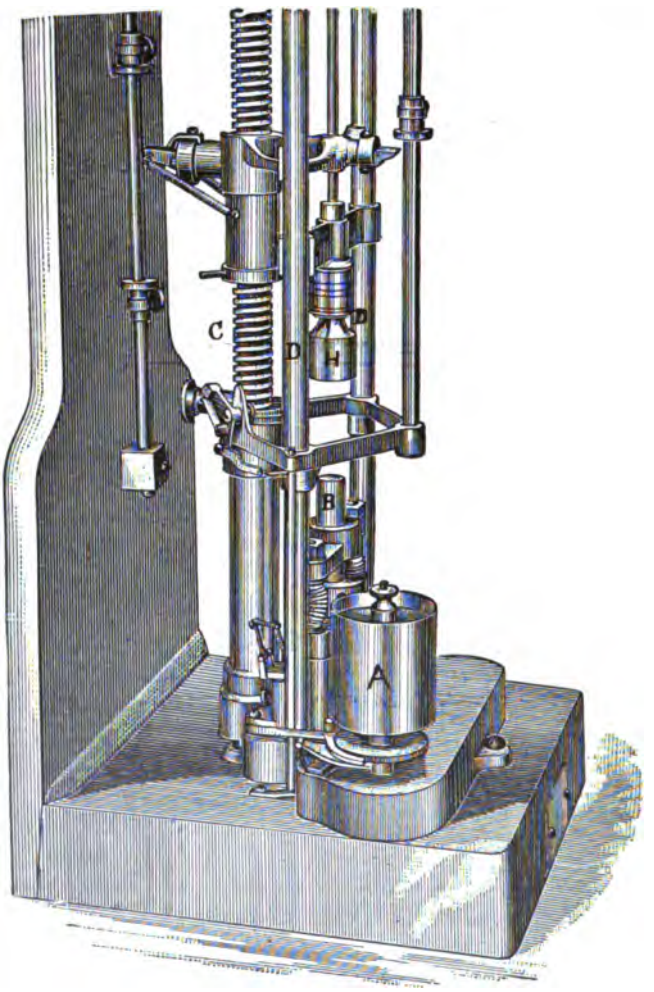


FIG. 4.

FIG. 5.

taken as representing the binding power of the stone, and is so used in comparing this property in different road materials. A

typical diagram (Fig. 5) is shown, in which complete failure occurred after 82 blows.

Tables II and II*a* exhibits some values for the abrasion and cementation tests conducted as described above.

TABLE II.

	Coefficient of Wear.	Cementation Test.
Trap rocks	5.7–26.1	1–16
Serpentine	5.8–21.2	10–300
Granitic and quartzitic rocks	2.6–16.3	1–13
Limestones	4.8–16.8	1–73
Sandstones	5 –13	0–28

In this table the figures signify :

Wear.	Cement.	Wear.	Cement.
1–7	1–4 bad.	12–17	10–20 good.
7–12	4–10 fair.	17–	20– excellent.

TABLE II*a*.

Locality of Quarry.	Name of Rock.	Wear. Coefficient.	Wear. Per Cent.	Commentation Value.
Amherst, Mass.	Diabase (trap).	20.33	1.97	62
Beverly, Mass.	Diabase (trap).	16.71	2.39	14
Boundbrook, N. J.	Basalt (trap).	18.61	2.15	16
Byram Station, N. J.	Basalt (trap).	26.93	1.49	31
Great Notch, N. J.	Diabase (trap).	18.59	2.15	36
Rockland Lake, N. Y. (opposite Sing Sing)	Diabase coarse (trap)	17.79	2.25	13
Lynn.	Diabase (trap)			
Meriden, Conn.	Diabase (trap)	15.49	2.58	28
Milton, Mass.	Diabase (trap).	22.77	1.75	34
West Springfield, Mass.	Diabase porphyry (trap).	22.14	1.81	17
Millington, N. J.	Trap.	19.64	2.04	53
Averages		19.91	2.06	30

It is important that the briquettes should be compressed in a uniform manner, and for this purpose the laboratory of the U. S. Department of Agriculture has designed a special machine (Fig. 6). The die is placed on an iron platform, supported by a piston rod, which is connected directly with a hydraulic piston below. Water from a tank is admitted to the hydraulic cylinder through a small orifice in the pipe. As the piston rises, the platform and die are carried up with it, the plug of the latter coming in contact with a yoke attached to a properly weighed lever arm. When the lever arm is raised one-eighth of an inch it closes an electric circuit, which trips a right-angle cock, shutting off the water, and opening

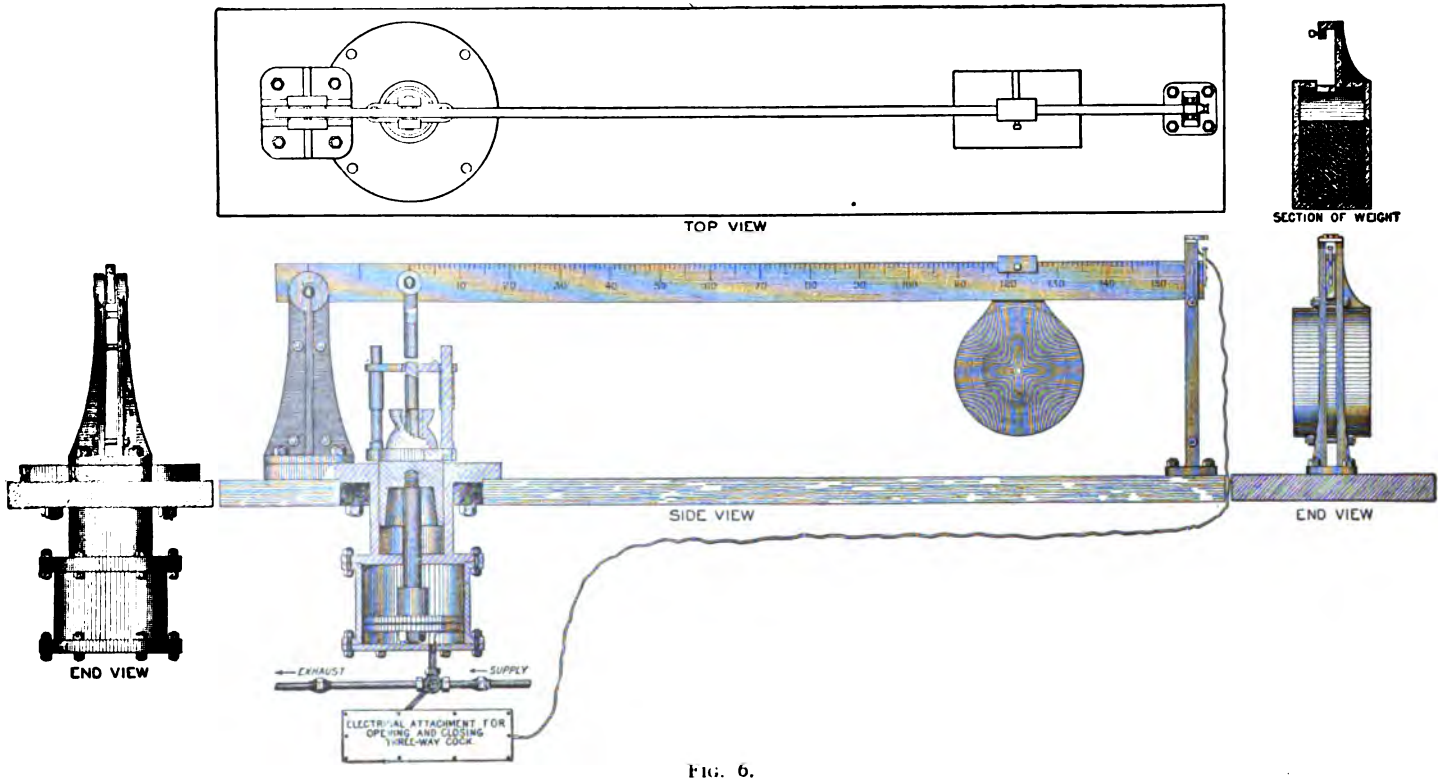

TOP VIEW
SECTION OF WEIGHT
END VIEW
SIDE VIEW
END VIEW
EXHAUST
SUPPLY
ELECTRICAL ATTACHMENT FOR OPENING AND CLOSING THREE-WAY COCK

FIG. 6.

the exhaust. About one minute is required to compress a briquette, and the maximum load is applied for an instant only.

Some of the details of the older impact-machine have also been modified for the purpose of securing greater convenience in operation.

Considerable difficulty has been experienced in keeping the briquette rigidly in place under the plunger, so that it should not be subject to lateral movements and complex stresses under the blows of the hammer. The usual device depended upon is a small brass plate fastened to the base of the machine, with a beveled hole slightly larger in diameter than the briquette; this has proved quite unsatisfactory, for the induced side thrusts frequently cause the lower edge of the briquette to crumble away under the successive blows, and failure of the test specimen to take place under too small a number of blows.

In the laboratory of the U. S. Department of Agriculture various clamping devises were tried and rejected. Finally the method was adopted of securing the briquette to the bed plate by means of shellac.

In preparing the stone dust for the cementation test, an automatic screen, about 100 centimeters long by 10 centimeters in diameter is used. It consists of a cylinder mounted on bearings at a slight angle with the horizontal, made of brass wire netting of two different meshes, 16 and 100 per linear inch, respectively. Into the upper end of the rotating cylinder the unscreened dust is automatically fed from a hopper, and in its passage is sifted into the two sizes. The upper end of the cylinder rests on wheel bearings, and on the bearing surface are several ridges which lift the cylinder whenever they pass over the wheels. This shaking device was introduced with the view of preventing the finer meshes of the screen from clogging. As the apparatus is completely covered, no dust can escape into the air.

In the laboratory at Columbia University, after repeated trials, the automatic screening device was found to be quite unsatisfactory, It clogged very rapidly, making it necessary to stop the machine frequently to clear the meshes; and the fine dust, getting between the bearing surfaces, caused surprisingly rapid wear. It was finally discarded, and hand screens in nests substituted, for separating the detritus of the cylinder charges into the two sizes which alone are needed for the purposes of these tests; namely, the portion

rejected by a 16-mesh sieve, for determining the amount of abrasion, and the portion passing through the 100-mesh sieve, for the cementation test. In compressing the briquettes, a simple hand lever machine is employed, which, being under perfect control, gives entire satisfaction.

The making of the briquettes, simple as it may seem, requires considerable skill and watchfulness, if the results of the test are to mean anything. The amount of water to be applied varies with the nature of the material, and can be determined only by trial. The object sought is to have the wet dust of the various specimens of the same consistency. With the small quantities of dust used for each briquette, a few drops more or less will vary the consistency quite noticeably, and with it, the degree of compacting of the mixture under the lever compression machine, which will inevitably appear in the variation of the results of the cementation test.

The quantity or weight of the dust to make a briquette of constant height can be determined also only by trial. Another factor which may cause to be incomparable the results of a cementation test made by the same or by different operators, was unexpectedly revealed during a series of tests made by the writer. Having occasion to repeat the cementation tests on two samples of road material, it was found that all the fine dust obtained by abrasion from those samples had already been used. An additional supply of the dust was therefore prepared, by breaking up the material in a mortar, and sifting to the proper degree of fineness. The results of the cementation test on the briquettes prepared from this dust varied so much from the original results, that a third series was made, using the dust obtained from the specimen on an iron rubbing board. These results differed materially from the other two. It would appear that the quantitative distribution of sizes of the particles of dust smaller than the mesh of the sieve varies with the mode of producing the dust. This, it is known from independent experiments, will affect the cementation value of the briquettes. Possibly also, the shape of the separate particles depends on the method of production, which would thus be another important factor in determining the cementing value of the specimen under test. This view was confirmed, later, by similar experiences in the laboratory of the Maryland Geological Survey, as described below. It was also noticed that the results of tests of briquettes

representing the same samples, made with all possible uniformity, varied considerably, when some of the briquettes were kept for the prescribed period of two weeks in the basement, and others in one of the upper offices of the building. This was undoubtedly due to unequal drying in the two cases.

When the fine abraded material of a given specimen is sifted, the finest particles pass through first, and what subsequently passes is coarser and coarser, until only a few particles of the "size of separation" of the sieve will pass. Unless the dust which has passed through the sieve is thoroughly mixed, the briquettes will give discordant results on a test, the finer material, in general, exhibiting greater binding power.

Another possible factor in causing the results of the cementation tests obtained in different laboratories to be incomparable was clearly brought out in the laboratory of the Highway Division of the Maryland Geological Survey. A quantity of thoroughly mixed dust from a certain specimen of rock was divided into two parts; one part was sent to the Massachusetts Highway Commission, and the part retained was sifted and molded into briquettes in the usual way, half of which were tested, and half sent to the Massachusetts laboratory. The dust sent to Massachusetts was treated in a similar manner — it was sifted and made into briquettes, half of which were tested there, and the other half sent to the Maryland laboratory. The briquettes made of the dust which had been passed through the sieve at the Maryland laboratory gave substantially the same resuts when tested at either place; whereas the briquettes made from the dust which had passed through the sieve at the Massachusetts laboratory gave results which, while differing from the former, showed substantial agreement at the two laboratories. From this it was concluded that the sieves in the two laboratories were not precisely similar, although they were supposed to be. This is a difficulty frequently encountered, especially with sieves of the finer meshes. On another occasion two samples of dust were prepared from the same stone, one in the course of the usual abrasion test, the other with pieces of iron placed in the cylinders. A microscopic examination of the sifted dust showed a distinct difference in the average sizes of the particles in the two cases; and the briquettes made from them showed a difference in strength, thus confirming similar observations made at the Columbia University laboratory. The above

considerations pointed conclusively to the necessity of devising some standard method of preparing the dust, and of having the sieves in the different laboratories practically alike. A *ball mill* (Fig. 7) was finally adopted as the standard for preparing the dust

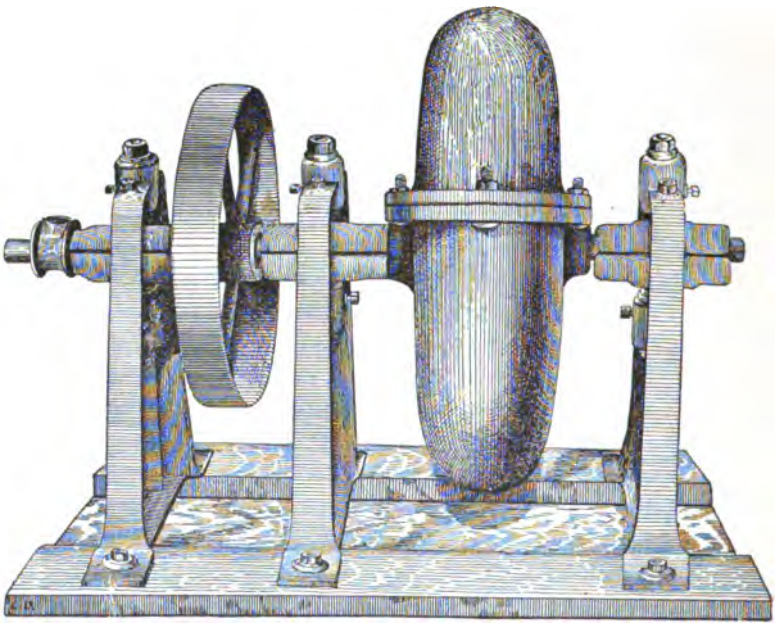


FIG. 7.

in a uniform manner. It consists of a flat, circular, cast-iron chamber containing two chilled-steel balls, weighing twenty five pounds each, and of slightly smaller radius than that of the rim of the chamber. One kilogram of rock fragments which will pass through a 6 millimeter opening, but not through a 1-millimeter opening, is put in the chamber and rotated for two and one half hours, making 5,000 revolutions. The ground material is then passed through a sieve made of No. 7 silk bolting cloth, with three meshes to the millimeter, and the briquettes are moulded from the dust passing through.

In molding briquettes for the cementation test, the Washington laboratory has modified the usual procedure. The fine dust is mixed with water and kneaded to the consistency of a stiff dough, which is kept in a closed jar for twenty-four hours. It is then made up in the usual way into briquettes, which are allowed to dry for twelve

hours in the air, and are then placed in a steam bath, where they remain for twelve hours. After cooling in a desiccator they are tested in the customary manner. This modification was suggested by the results of certain experiments, which showed that the cementing value increases progressively if the dough made from the rock dust is allowed to stand for some time before being molded; and the increase is greater if the dough had been previously well kneaded. This point was clearly brought out in a series of tests made on three typical specimens of stone, representing road material of good, medium and poor cementing value, and the results, which were plotted for convenience of study (Fig. 8), showed that there

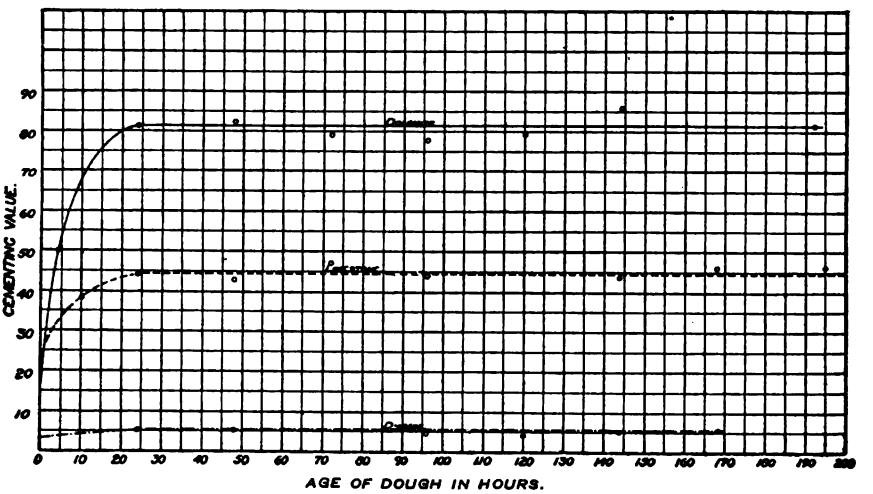


FIG. 8.

occurred in each case a rapid rise in cementing value up to the age of twenty-four hours, after which it remained practically constant. These observations are of considerable practical importance, as will appear later.

Tests of many varieties of rock dust showed that the more finely they were pulverized the higher would be their cementing value when molded under pressure, either with or without moisture; and the greater the pressure, the higher the value. Of two sets of briquettes made with the same rock dust, one molded wet, the other dry, the former invariably yielded the higher result; and, within certain limits, the more wet the material, the higher the

cementing value. That this is not due to a chemical change induced by the action of water, has been shown by testing briquettes made of pulverized glass mixed with alcohol, which yielded like results. It was formerly thought that the water added to a rock dust acted merely as a lubricant to the fine particles, allowing them to slide over each other more easily under pressure, and thus mechanically interlock.

It has often been observed that specimens of some rocks known to consolidate well under traffic in a short space of time, and to produce a very serviceable road surface, would yield low results under the usual cementation test in the laboratory. Anomalous results such as this, and others equally unsatisfactory (some of which have been referred to above, while others will appear in a subsequent discussion on recementation), induced the Road Material Laboratory of the U. S. Department of Agriculture to investigate the cause, or causes, of the cementing properties which exist in many rock dusts; some results of this study have already appeared in a paper published in the *Journal of the American Chemical Society*, for May, 1903, and in Bulletin No. 85, Bureau of Chemistry, U. S. Department of Agriculture, August, 1904. It appears that the cementing value depends upon a hydrated colloidal condition of the particles, or of some proportion of the particles, which is the result of certain secondary changes produced in the minerals composing the rock structure. This property seems to be closely related to that of the plasticity of clays, and to be due to the presence of certain amorphous inorganic particles, which, by reason of their characteristic porous structure, are able to absorb and hold water, thereupon assuming a plastic and adherent condition. Generally speaking, this action commences the moment water is added to the dry dust, and is most active in the early stages of mixing and kneading; it thus happens that considerable errors in the cementation tests may result from small variations in the time of molding the briquettes after the water has been added, as is clearly shown in Fig. 7. The modifications of the usual method of preparing briquettes, introduced in the Washington Laboratory, would therefore seem to be well founded, and to be conducive to greater uniformity and comparability in results.

Until quite recently the cementation values have been obtained by the method first described in this article, and most of the published reports of such tests must be read with this understanding.

TABLE III.

CEMENTING VALUES OF SAMPLES OF CHERT BY THE OLD AND NEW METHODS.

Serial No.	Locality.	Cementing Values.	
		Old Method.	New Method.
338	Graytown, Tenn.	24	240
342	Near Columbia, Tenn.	148	1,083
389	Birmingham, Ala.	10	84
391	" "	35	127
392	" "	26	113
393	" "	6	58
394	" "	26	102
388	" "	8	31
443	" "	118	390
414	Walker County, Ga.	2	12
418	" " "	9	35
438	Hot Springs, Ark.	2	10
538	San Jose, Cal.	9	13
360	Blue Springs, Neb.	17	102
584	Elco, Ill.	4	15
437	" "	12	72

TABLE IV.

RANGE OF CEMENTING VALUE IN DIFFERENT ROCK SPECIES.

Kind of Rock	Number of Samples.	Maximum.	Minimum.	Average.
Amphibolite	8	36	3	10
Andesite	3	337	14	129
Basalt (trap)	22	500	2	91
Chert	19	500	2	101
Conglomerate	3	327	12	154
Dolomite	20	161	2	31
Diabase (trap)	39	110	2	26
Diorite (trap)	13	137	1	20
Eclogite	5	20	1	7
Felsite	7	101	2	34
Flint	1	31	31	31
Gabbro	8	131	3	30
Gneiss	22	21	1	6
Granite	37	77	1	10
Pyroxene granulite	1	1	1	1
Limestone	77	231	4	63
Marble	1	5	5	5
Peridotite	1	3	3	3
Quartzite	10	9	1	4
Rhyolite	9	500	1	152
Sandstone	26	323	1	63
Schist	25	272	1	23
Shale	3	500	62	314
Slate	2	202	151	176
Syenite	2	11	2	7

Table III. has been introduced for the purpose of showing the great differences in cementing values that may be obtained by the two methods of procedure outlined above.

Table IV. shows that considerable variability in cementing value is to be expected in rocks of the same species; and that high values of this useful property are not confined to any one group.

The cementation test as practiced at present is not entirely satisfactory, although the modifications introduced in the Washington laboratory constitute a notable advance. It is difficult to obtain uniform and comparable results; and, further, it would appear desirable that the character of the test specimen should approximate, as nearly as may be practicable, the condition of the material on the roadway. This may be approached by making the briquettes of a mixture of the fine dust, obtained as usual, and a definite quantity of some aggregate, preferably coarser particles of the same sample, sifted to some standard degree of fineness. The best proportional quantities, and the best size of aggregate to be used, can be determined only after numerous comparative experiments. The size of the test specimen might well be made larger, to reduce the influence on the result of small accidental defects in the piece. It is entirely analogous to the testing of briquettes of hydraulic cement made neat, or with the proper admixture of a standard sand, the latter giving the more valuable and practical information.

Furthermore, since the surface of a broken stone road is being constantly abraded, dried, moistened, and recemented, it would seem to be desirable to also determine the *recementing* properties of the specimens, thus furnishing additional information of special

TABLE V.

COMPARISON OF CEMENTING AND RECEMENTING VALUES.

Serial No.	Name.	Cementing Value.	Recementing Value.
335	Diabase (trap)	110	89
336	Ferruginous limestone	158	72
337	Dolomitic limestone	59	42
338	Novaculite (chert)	24	18
340	Limestone	95	29
343	Dolomite	32	23
344	Sandstone	54	23
349	Diabase (trap)	49	44
346	Limestone	8	13
351	Gravel	11	13
383	Limestone	22	34
403	Limestone	110	126
492	Dolomitic limestone	22	30
497	Hornblende schist	7	9

practical significance. Formerly this was done in the following manner: a set of briquettes of *constant weight* instead of constant height, was made and tested, and the broken down material was made into a new set of briquettes, and again tested to failure. The number of blows in the second case gave the value of the recementing power of the fine dust.

In most cases, the recementing values were found to be smaller than the corresponding cementing values (Table V.), the exceptions receiving, in some cases, at least a partial explanation in the colloidal theory of the cementing value of rock dusts. Indeed, this theory of the underlying cause of binding power is sufficient to account for many otherwise perplexing results encountered in the course of testing road materials in the laboratory; and it has already led to several necessary modifications in the usual method of procedure, to insure greater reliability in the results.

In Tables VI. and VII. are given values for abrasion and cementation obtained in the laboratory of Columbia University. The cementation values were obtained by the method of testing first described.

Table VII. has already appeared in the annual report of the N. Y. State Engineer and Surveyor.

Toughness Test. — This test is made on 25 millimeter by 25 millimeter rock cylinders, with the impact machine used for testing the briquettes of rock dust. Instead, however, of a flat-end plunger resting on the test piece, as in the cementation test, a plunger with the lower end bearing surface of spherical shape, having a radius of 1 centimeter, is used. It can be seen that the blow as delivered through a spherical-end plunger approximates as nearly as practicable the blows of traffic, and it has the further advantage of not requiring great exactness in getting the two bearing surfaces of the test piece parallel, as the entire load is applied at one point on the upper surface. The test piece is adjusted so that the center of its upper surface is tangent to the spherical end of the plunger, which is pressed firmly upon the piece by two spiral springs surrounding the plunger guide rods. The cylinder is held to the base of the machine by a device which prevents its rebounding when a blow is struck by the hammer, which weighs 2 kilograms. The test consists of a 1-centimeter fall of the hammer for the first blow, and an increased fall of 1 centimeter for each succeeding blow until failure occurs, the *number of blows* required to cause failure being

taken to represent the toughness. The cylindrical test pieces may be made with a core saw designed for the purpose.

Resistance to Crushing. — An Emery Hydraulic machine, with a capacity of 150,000 pounds, and a Riehlé machine, with a capacity of 100,000 pounds, are available for use in tension, compression, or cross-bending tests. The *ultimate compressive resistance* of cubes

TABLE VI.

	Wear.		No. of Tests.	Average Cementation Values.
	Coefficient.	Per cent.		
Diabase.	16.81	2.38	6	56
"	14.90	2.68		
"	14.39	2.78	6	18
"	15.99	2.56	5	56
"	14.55	2.75		
Sandstone.	8.09	4.94	6	19
"	9.08	4.40		
"	9.64	4.15	6	11
"	9.08	4.40		
"	6.78	5.89	7	10
"	6.97	5.74		
"	11.43	3.50	7	4
"	11.58	3.46		
"	9.04	4.43	4	43
Limestone.	9.08	4.40	6	4
"	13.44	2.98	7	5
"	11.84	3.38		
"	9.38	4.26	6	2
"	9.97	4.01		
"	6.32	6.32	6	12
"	6.41	6.24		
"	5.42	7.37	2	11
"	4.91	8.11		
"	8.68	4.60	5	30
"	8.82	4.53		
"	7.04	5.68	4	0
"	6.32	6.33		
"	9.67	4.13	4	0
"	8.38	4.78		
"	7.18	5.58	4	51
"	7.41	5 40		
"	9.21	4.34	4	13
"	9.13	4.38	4	10
"	8.20	4.88	6	18
"	7.98	5.01		
"	10.22	3.91	5	23
"	10.30	3.88		
"	7.77	5.15	7	12
"	7.63	5.24		
"	9.22	4.34	6	40
"	9.12	4.39		
"	7.80	5.13	6	28
"	8.01	5.00		
"	13.01	3.17	6	48
"	13.35	3.00		

TABLE VII.

Locality of Quarry.	Name of Rock.	Wear. Coefficient.	Wear. Per cent.	Cementation Value.	Where Used.
Albany County, N. Y. Quarries ½ mile north from Dunsbach Ferry station on N.Y.C.&H.R.R.R. on S. side of Mohawk river...	Hudson river sandstone.....	6.78	5 96	50	Used for top and base of section 2 of Loudon road. No. 119, from Albany to Cohoes, built during 1903 by the State.
Chemung County, N. Y. Wells Quarry, 3 miles west of Elmira, N. Y.....	Chemung grit....	5.82	6.88	24	Used during 1901 for base of 3½ miles of the Southport road to the south boundary of New York State, built by State.
Chenango County, N. Y. From ledge 5 miles north of Norwich, on farm of Loren Cushman, 300 feet west of Norwich and Plymouth road No. 112	Sandstone	6.80	5.88	26	Used during 1902 for base top 2 miles of Norwich and Plymouth road No. 112, built by State.
Cortland County, N. Y. From ledge on farm of O. G. Kellogg, 2½ miles S. E. from Cortland, N. Y	Calcareous sandstone	7.07	5.65	30	Used during 1902 for base of 1 mile of road south from Cortland, Blodgett's Mills road, No. 111, built by State.
Clinton County, N. Y. Plattsburgh, Clinton county, N. Y., Moore's Quarry, north side of village	Clinton blue limestone	6.87	5.82	11	Used during 1901 for base and top and filler of $\frac{1}{10}$ mile of Plattsburgh and Keeseville road, built by State.
Five miles south of Plattsburgh, N. Y., quarry on north bank of Salmon river	Clinton gray limestone	10.94	3.66	25	Used during 1901 for base and top and filler of 2½ miles of Plattsburg and Keeseville road, built by State.
Dutchess County, N. Y. Clinton Point, near Poughkeepsie.....	Gray limestone...	13.80	2.90	39	Used for base of 9 miles of road in Eastern New York built by the State in 1899 and 1900, and also for base and top of many roads in vicinity of New York city

TABLE VII.—*Continued.*

Locality of Quarry.	Name of Rock.	Wear. Coefficient.	Wear. Per cent.	Cementation Value.	Where Used.
Erie County, N. Y. Buffalo Cement Co. Quarries, in north part of city of Buffalo	Buffalo Plains limestone, with little embedded flint	8.29	4.82	67	Used for base and top of 33 miles of 16-foot roadways in ten cities and towns of Western New York during years 1893–1900; used for base of six miles of State road near Buffalo.
	Buffalo Plains limestone with much embedded flint	9.66	4.14	94	
Genesee County, N. Y. LeRoy, Genesee county, N. Y., N. B. Keeney & Son's quarries	Onondaga gray limestone	10.87	3.68	21	Used during 1901 for base of 1 mile of Orchard Park road, Erie county, and for base of 1 mile of Pittsford road, and of 1½ miles of Fairport road in Monroe county, and for filler for several other roads built by State.
Ditto	Onondaga gray limestone	11.04	3.62	15	
Ditto	Onondaga gray limestone	10.70	3.74	21	
Herkimer County, N. Y. Little Falls, Herkimer Co., Moss Island, Mohawk river	Hornblendic gneiss	5.16	2.64	10	Used for base and top of 1 mile of Frankfort and Utica road, built by State in 1900.
Town of Warren, Herkimer county, N. Y., J. W. Packer's quarry	Crystalline limestone	7.63	5.24	21.5	
Madison County, N. Y. Perryville, Madison Co., N. Y., Cyrus Warlock's quarries, on Canastota branch of the Lehigh Valley R. R.	Onondaga gray limestone	7 99	5.00	24	Used during 1901 for base and top and filler of half mile of road built by State at Truxton, Cortland Co.
Monroe County, N. Y. Glacial drift field stone near Rochester, Monroe county	Red sandstone	9.03	4.43	16	Used for base of Little Ridge road west from Rochester, 6 miles, built by State during 1899 and 1900.
Glacial drift field stone near Rochester, Monroe county	White sandstone	11.05	3.62	24	
Rochester, Monroe county, N. Y., Goodman street quarries of Foery & Kastner	Niagara gray limestone	7.22	5.54	42	Used during 1902 for base and top and filler of section 1, Webster road, No. 98, 1⅝ miles from Clifford street, Rochester, to Irondequoit creek, Monroe county, N. Y., built by the State.

TABLE VII.—*Continued.*

Locality of Quarry.	Name of Rock.	Wear. Coefficient.	Wear. Per cent.	Cementation Value.	Where Used.
Montgomery County, N. Y.					
Quarry on north side of Mohawk river, near Yosts, Montgomery county, N. Y.	Calcareous sandstone	6.42	6.23	11	
Oneida County, N. Y.					
Two miles S. E. of Utica, N. Y., from Seaton Quarry, Oneida county, N. Y.	Red and Yellow sandstone, loose-grained	6.57	6.09	8	
Ditto	Gray sandstone and quartz conglomerate, close grained	7.04	5.68	12	
Franklin Iron Works, Kirkland, Oneida county	Slag	2.73	14.62	28	
Onondaga County, N. Y.					
Seneca Clark Quarry, 12 miles south of Syracuse, near Lafayette, Onondaga county, N. Y.	Gray sandstone	5.97	6.69	68	
National Wall Plaster Co., Jamesville, Onondaga Co., N. Y.	Limestone	10.95	3.65	15	
Alvord Quarries, near east line of town of Onondaga, Onondaga county	Blue limestone	9.14	4.38	89	
Split Rock Quarries Solvay Process Co., town of Onondaga, also Indian quarries, on N. E. part Onondaga Reservation, also Jamesville Quarries near Penitentiary of Onondaga county, N. Y.	Gray limestone	6.20	6.45	22	Used for base of 2 miles of James street and Cortland street roads, near Syracuse, built by State in 1899 and 1900.
Indian Quarries, overlying the gray, on N. E. part Onondaga Reservation	Blue limestone	5.99	6.68	33	
Rockland County, N. Y.					
Rockland Lake, N. Y., quarries of Rockland Lake Trap, Rock Co. (Conklin & Foss) opposite Sing Sing, on the Hudson River	Diabase (trap) coarse	14.62	2.74	35	Used during 1900 and 1901 for top of 2 miles and for base and top of 1 mile of Loudonville road, built by State north from Albany.

TABLE VII.—*Continued.*

Locality of Quarry.	Name of Rock.	Wear. Coefficient.	Wear. Per cent.	Cementation Value.	Where Used.
St. Lawrence County, N. Y.					
From the dark quarries of the Northern New York Marble Company at Gouverneur, St. Lawrence, County, N. Y.....	Dark blue crystalline limestone or marble.	4.72	8.47	13	
From the light quarries of the Northern New York Marble Company at Gouverneur, St. Lawrence County, N. Y.....	Light gray crystalline limestone or marble.	6.56	6.11	18	
Saratoga County, N. Y.					
Six miles S. W. of Glens Falls, N. Y., Slades Quarry —from north end of quarry.	Gray and black granite.....	9.30	4.30	7	Used during 1901 for base of 3½ miles of Glens Falls and Saratoga road, built by State south from Glens Falls.
Ditto from center of quarry.	Gray granite.....	10.88	3.68	8	Top of ditto.
Schoharie County, N. Y.					
Schoharie, Schoharie Co., N. Y., quarries of Riley & Mix.....	Lower Helderberg blue limestone.....	9.00	4.45	40	Used during 1902 for base and top and filler (with sand) of 1¼ miles Delmar and Slingerland road No. 92 and for part of base and for top and filler of 1¾ miles of North road No. 124, both built in Albany Co. by the State.
Ulster County, N. Y.					
Bluestone Quarry, near Phœnica, Ulster county, N. Y.....	Blue sandstone..	11.17	3.58	39	Used for base and top of 10 miles of Ulster and Delaware road, built near Phœnicia by State in 1900 and 1901.
Water-worn stones from bed of Esopus creek, near Phœnicia, Ulster county, N. Y. (similar to the quarry stones)	Blue sandstone..	10.42	3.84	11	
Smith & Post Quarry, West Catskill, N. Y.....	Sandstone, Esopus grit.....	8.52	4.69	60	
Turtle Pond Quarry, Kaaterskill, N. Y.....	Shaley gray New Scotland limestone.....	10.09	3.96	68	

TABLE VII.—*Continued.*

Locality of Quarry.	Name of Rock.	Wear.		Cementation Value.	Where Used.
		Coefficient.	Per cent.		
Holdridge Quarry, Kaaterskill, N. Y.	Becraft reddish gray crystalline limestone	7.61	5.25	56	
Westchester County, N. Y.					
On east side of Kensico reservoir at roadside	Gray quartzite	11.13	3.59	9	Used during 1900 and 1901 for base of 3¾ miles of White Plains and Armonk road, built by State.
Near Elmsford, N. Y., spoil-bank of shaft No. 12 excavated from Croton Aqueduct tunnel in 1888	Quartzite	6.77	5.90	15	Used during 1900 and 1901 for base of Sawmill River road, built by State.
One-half mile north of East View, N. Y., Rockefeller Quarry at roadside	Dark gray granitic rock	10.06	3.98	10	Used during 1901 for base of roads north and south from Eastview, built by State.
Two miles west from Bedford, ledge at Light's farm	Pink and gray gneiss	8.64	4.63	12	Used during 1901 for base of two miles of road between Mt. Kisco and Bedford, built by State.
Yates County, N. Y.					
Dresden, Yates county, N. Y., quarries of Seneca Lake Broken Stone Co., producing naturally fractured stone	Hamilton gray limestone	6.99	5.76	26	Proposed for use in building roads in vicinity.
New Jersey Rocks.					
Millington, N. J., quarries of Morris Co. Crushed Stone Co	Basalt (trap)	18.57	2.15	.....	Used during 1895–1901 for 50 miles of roads in Morris, Somerset and Union counties, New Jersey.
Bound Brook, N. J., quarries of Bound Brook Crushed Stone Co	Basalt (trap)	19.27	2.08	.....	Used for roads in vicinity of Bound Brook, Somerville and New Brunswick, New Jersey.
Great Notch, N. J., quarries of Francisco Brothers	Basalt (trap)	16 00	2.59	205	Used during 1902 for top of 2 miles of Lestershire road, No. 125, Broome county, N. Y., built by the State.

of the material is determined in the usual manner, and is expressed, generally, in pounds per square inch. Occasionally the French coefficient is employed. It is derived from the consideration that cubes of the hardest rocks used in road building rarely exhibit an ultimate compressive resistance greater than 3,000 kilograms per square centimeter; to rocks possessing that degree of compressive strength is assigned the coefficient 20, for the sake of uniformity with the standard coefficient in the case of the cementation tests; and other rocks receive ratings corresponding to their compressive resistances.

Petrographic Examination. — For a complete report on a sample of rock, and in some cases, in order to properly classify it, a microscopic examination of its structure should be made. This can be conveniently accomplished by preparing one or more very thin sections of the material. Such sections, under the microscope, exhibit great variety of structure in different rocks, and are both interesting and instructive. In some crystalline rocks, for example, they show clearly the kinds and sizes of crystals, and the way they are intertwined or interlocked, thus accounting, in a measure, for their toughness. The minerals of other rocks, as the gneisses and some granites, are not interlocked; such rocks crumble comparatively easily. The strength of quartzites, composed of quartz particles held together by some cementing material, but not interlocked, will depend on the strength of the cementing material; and so on. The amount of *absorption*, the *specific gravity*, and the *weight per cubic foot* of the sample are determined in the customary manner.

In addition, there is available the necessary apparatus for testing, under standard conditions, samples of paving brick, and of paving blocks of stone and wood.

The laboratory is also properly equipped for investigations in the nature and physical properties of limes, mortars, cements, and concretes, as well as for the ordinary practical testing of such materials.

In conclusion, the author wishes to acknowledge his indebtedness for much valuable information obtained from the reports issued by the Laboratory for Testing Road Materials, U. S. Department of Agriculture; the Laboratory of the Maryland Geological Survey, Division of Highways; and the Laboratory of the Massachusetts Highway Commission. In this article he has freely quoted from the pages of their reports, particularly in the descriptions of apparatus and methods of operation. Most of the illustrations, and Tables I to V inclusive are from the same sources.

THE RETARDATION METHOD OF MEASURING LOSSES IN ELECTRIC MOTORS AND GENERATORS.

By Frederick W. Seringhaus, Jr., and Gerard B. Werner.

Introductory.

Besides the Prony brake, the stray-power, and the Hopkinson methods for determining the efficiency of dynamo-electric machinery, a new test has recently been introduced, which commends itself on account of several inherent advantages. The test is known as the Retardation Method of measuring losses, and is at present employed in the testing department of the General Electric Company. It was first suggested by M. Routin in *L'Eclairage Electrique*, Vol. IX., p.169 (1896). Descriptions of some modifications of this method appeared in the (English) *Electrical Review*, Vol. XLVII., p. 287 (1900), and in the *Electrotechnische Zeitschrift*, Vol. XX., p. 274 (1899).

At the suggestion of Prof. G. F. Sever, the merits of this retardation method were investigated by the authors in the laboratories of the Electrical Engineering department of Columbia University. The results are given in detail in the following pages.

1. *Fundamental Principle.* — The armature is first run up to speed and the driving power is cut off; it is then allowed to come to rest while at small intervals of time, the speed is measured directly or indirectly. The speeds in revolutions per second or in radians per second are plotted with respect to time. At any given moment let ω be the angular velocity, and let a tangent be drawn to the curve at the point corresponding to the moment in question. The tangent then measures the time rate of change of the angular velocity, or $d\omega/dt$ the angular retardation. Let the moment of inertia of the revolving part in C.G.S. units be denoted by I. At any moment the rate of change of its angular momentum, $I\omega$, is equal to the retarding torque acting on it in C.G.S. units; or

$$T = -I\frac{d\omega}{dt}$$

and the rate at which the stored rotational energy, $\frac{1}{2} I \omega^2$, is expended in overcoming the retarding torque is $-I\omega\, d\omega/dt$ ergs per

second, or $-I\omega\, d\omega/dt \times 10^{-7}$ watts. This latter expression is equal to the rate at which energy is dissipated in (*a*) friction, (*b*) windage, (*c*) hysteresis, (*d*) eddy currents. Thus if the retardation curve is determined and plotted (1) with field excited and brushes down, (2) with field unexcited and brushes down; and (3) with field excited and brushes up, a complete analysis of the various losses may be made.

If the machine under test is a motor, the field excitation being constant, and the efficiency curve is required from no-load to a fraction overload, the speeds corresponding to successive loads must be determined from a brake test; in order that the stray power losses may be determined for the proper condition. Similarly, if the machine under test is a generator, the armature characteristic of the machine must be obtained in order that the various speeds at which the losses should be determined may be known.

2. *Description of Test.*— The machine is run without load as a separately excited motor. After the armature has been run up to a convenient speed, the armature current is switched off (the field being maintained at full excitation from an independent source throughout) and the armature allowed to slow down. The speed at any moment was taken to be proportional to the voltage generated by a small dynamo with permanent field magnets, directly connected to the shaft of the machine under test. As the pointer of the voltmeter passed over a certain scale-division, taken as the initial reading, a stop-watch was started. This was stopped again when the voltmeter reading had diminished a certain amount. The machine was once more run up to speed, the current switched off, and the stop-watch started at the same initial voltmeter reading as before, and stopped at a lower reading than in the first case. By this means the time interval taken by the armature to come down to a number of different speeds from a certain initial speed could be determined.

In the first trial, accurate readings were made possible by prolonging the time taken by the armature to come to rest, by affixing a large heavy flywheel to the shaft. In the second trial, the retardation was automatically recorded on a strip of uniformly-moving paper by two small electro-magnets, one of which, connected to the clock circuit, marked seconds, and the other of which marked revolutions.

Three curves were determined: (1) with field excited, brushes

down; (2) with field unexcited, brushes down; and (3) with field excited and brushes off. From each curve the value of $d\omega/dt$ or $2\pi\, dn/dt$ was evaluated by drawing a tangent to the curve at the point corresponding to the speed (ascertained from the brake test if the machine is a motor, or from the armature characteristic determination, if the machine is a generator), at which the loss is to be determined. The loss in watts in each case is

$$W = 4\pi^2 In \frac{dn}{dt}$$

in which n is in revolutions per second. This expression found from curve (1) gives the total stray power losses. The corresponding expression found from curve (2) — at the same speed — gives the friction losses; the difference between the total stray power losses and the friction loss giving the core losses. The expression found from curve (3) — at the same speed — gives the loss in bearing and air friction plus the core losses. The core losses having been found, the bearing-friction loss is obtained by subtraction; likewise the brush friction loss is the difference between the total friction loss and the loss in bearing friction.

The eddy-current loss may be separated from the other losses by assuming that the hysteresis and friction losses are proportional to the speed and the eddy-current loss proportional to the square of the speed; *i. e.*,

$$4\pi^2 In \frac{dn}{dt} = An + Bn^2$$

or,

$$4\pi^2 I \frac{dn}{dt} = A + Bn$$

where A is the constant for hysteresis and friction, and B the constant for eddy-currents. To obtain the values of A and B a curve is plotted between dn/dt and n — with brushes off —; and from the curve, the point at which the curve tends to cut the axis of no speed is found. That is, the value of dn/dt when $n = 0$ is obtained. Then

$$A = 4\pi^2 I \frac{dn}{dt}$$

and An = loss in hysteresis and bearing friction. Subtracting from the values of An, the loss in bearing friction at corresponding speeds,

the hysteresis loss is obtained; and the difference between the core loss and the hysteresis loss will give the eddy-current loss.

3. *Method for Determining the Moment of Inertia of the Rotor.*— The quantity I may be determined from the retardation curve previously plotted as follows: When the machine is running as a separately-excited motor, let the power supplied to the armature be carefully measured. The input to the armature (at no-load) minus the power lost in heating the armature coils represents the power employed in turning the armature against the various torques (*i. e.*, the counter-torques due to hysteresis, eddy-currents, windage, and friction). Let this "driving power," expressed in watts, be denoted by w; then if ω is the angular velocity of the rotor at which the input has been taken, and $d\omega/dt$ the corresponding angular retardation (found from the retardation curve)

$$10^7 w = I\omega \frac{d\omega}{dt}$$

or

$$I = \frac{w \times 10^7}{4\pi^2 n \frac{dn}{dt}} \text{ C.G.S units}$$

where

$$w = C(E - Cr_a).$$

Readings of the armature current when the machine is running at different speeds should be taken in order that the calculations may check. For a satisfactory set of readings, the bearings must be in a steady state (the machine ought to run 2 to 3 hours before the test) and a plentiful supply of lubricant is essential.

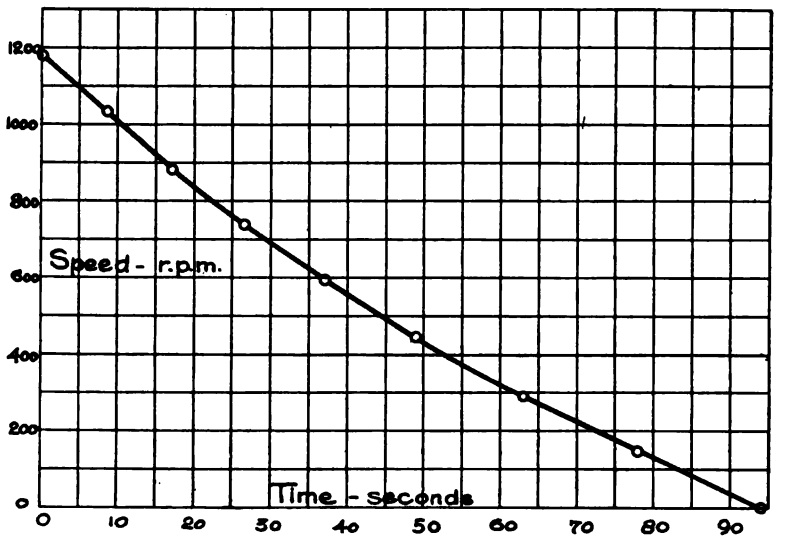
4. *Conclusions, Discussion of Results, etc.*—(*a*) From the tabulations, it will be seen that the values found for the *moment of inertia* check very closely, the mean difference between the actual values and the value assumed being about .3 per cent. in the case of the armature and flywheel, and .7 per cent. in the case of the armature alone.

(*b*) An ordinary *stray-power test* was made on the same machine under as nearly identical conditions as could be attained, for the purposes of *comparison with the retardation method.* The results are shown in Table VIII. The agreement of the values of the retardation test with those of the stray-power test is about 99.4 per cent.—the mean error, .6 per cent., being within the probable errors of observation and calculation.

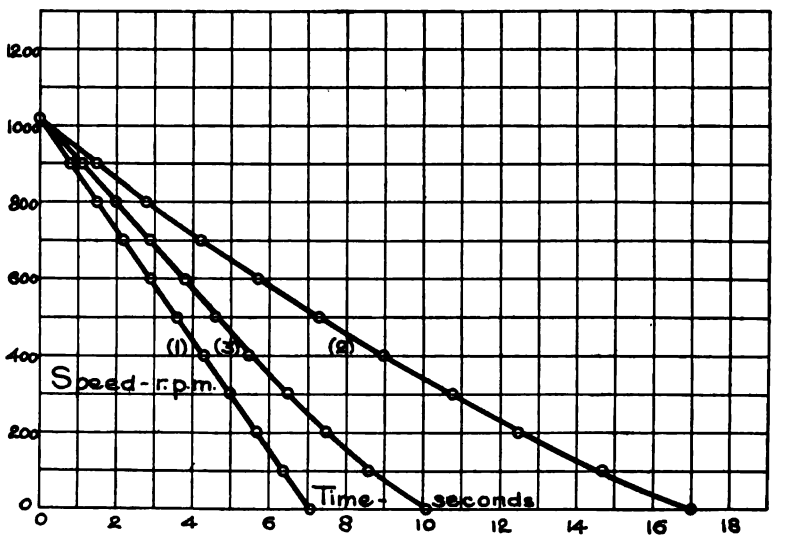
(*c*) The crucial point determined in this trial is the fact that *the retardation curve from the point of initial speed* (*i. e., zero time*) *to a point half-way down the curve, is a straight line*, as found both from the readings taken with a .1-second stop-watch and Weston voltmeter and auxiliary dynamo used as a speed indicator, and from the automatic record made by the apparatus alluded to in Par. 2. This point above which the curve is a straight line was found (from the average position on ten different curves) to be 48 per cent. from the initial speed — that is, from the initial speed to a point where the speed is about 50 per cent. smaller, the retardation is constant, dn/dt having but one value for all values of n within those limits.

(*d*) *The separation of the eddy-current loss from the hysteresis loss* can be only approximate, inasmuch as the basis (*i. e.*, the prolongation of the dn/dt curve) of this calculation is purely graphical and subject to a variety of constructions. The values found can be checked only when the thickness of the armature sheets, the flux-density, in the iron, and the hysteresis constant are known.

(*e*) There are two fundamental and inherent *advantages in the retardation method* of testing for losses. First, a complete analysis of the losses of the machine, including the separation of the eddy-current and hysteresis losses may be made without another machine to operate the one under test. All that is needed is a supply circuit of the same voltage as the machine tested. Thus, to separate the friction loss from the core loss *experimentally* (the core losses being capable of being determined by calculation if sufficient data is available) without the aid of the retardation method, the machine tested must be run by a second machine, the difference in the watts required to operate the auxiliary machine when the field of the first machine is excited and unexcited being the core loss. Secondly, since with a certain field-strength, and from a certain initial speed, the time required by the armature to come to rest is fixed, any decrease in this period of slowing down will indicate an increase in the inherent retarding torques of the machine, and hence an increase in the losses. Thus, for regular periodical tests it is only necessary to fix definitely the duration of time required by the armature to go from some fixed speed to standstill with a fixed field magnetization. A good idea can be obtained of the condition of the machine without the use of any instruments other than a stop-watch.



I. *Retardation curve* (with flywheel).
1 H.P. Generator.
$I = .713 \times 10^7$.
Field excited — .23 ampere.
Brushes down.



II. *Retardation curves* (without flywheel).
1 H.P. Generator.
$II = .0895 \times 10^7$.
(1) Field excited, brushes down.
(2) Field unexcited, brushes down.
(3) Field excited, brushes up.

5. *A suggestion for a laboratory experiment.* — The modification of the test which would make the same adapted to laboratory purposes consists in determining the upper quarter, instead of the entire retardation curve. Let *one* point at about three-quarters of the rated speed of the machine, be determined accurately by several readings. The point found will lie on the straight-line portion of the curve. The natural variations in speed will be above this lower limit of the curve and there will be but one value of the retardation, dn/dt, for all values of the speed n, corresponding to different loads. Let three curves be plotted as enumerated in paragraph 1, and the brush-friction, bearing-friction and windage, and core losses (the latter in aggregate) be determined.

I. STRAY POWER TEST.

e. m. f.	Armature Amperes, Load.	Field Amperes.	Armature Amperes, no Load.	Speed r. p. m.	Watts, no Load.	Watts C^2R_a	Stray Power, Watts.
112	0	.23	1.30	1025	145.5	2.06	143.4
114	.96			1045	148		145.9
118	1.84			1065	153.3		151.2
120	2.75			1085	156		153.9
122	3.66			1095	158.5		156.4
124	4.57			1115	161		158.9
124	5.48			1125	161		158.9
126	6.44			1150	163.8		161.7
128	7.30			1160	166.4		164.3

C^2R_a Load.	C^2/R_f	Total Losses.	Watts.		Per cent. Efficiency.
			Input.	Output.	
0	2.2	145.6	145.6	0	0
1.11		149.2	254.2	105	41.3
4.13		157.5	360.0	202.5	56.1
9.24		165.3	467.8	302.5	65.0
16.35		175.0	577.5	402.5	69.8
25.5		186.6	689.6	503.0	73.0
36.6		187.7	800.2	602.5	75.4
50.7		214.6	922.6	708.0	76.7
65.2		231.7	1034.7	803.0	77.6

$$\begin{cases} R_a = 1.22 \text{ ohms.} \\ R_f = 41.5 \text{ ohms.} \end{cases}$$

II. MOMENT OF INERTIA ARMATURE AND FLYWHEEL.

n	ω	$\frac{dn}{dt}$	$\frac{d\omega}{dt}$	Watts.	I
14.6	91.7	19/73	1.635	118.3	$.723\times10^7$
12.3	77.3	18.6/78	1.500	82.5	$.713\times10^7$
9.75	61.3	17.9/81	1.39	60.3	$.708\times10^7$

III. Moment of Inertia Without Flywheel.

n	$\frac{dn}{dt}$	Watts.	I
17.1	2.4	143.4	$.0887 \times 10^7$
17.4		145.9	$.0888 \times 10^7$
18.3		156.4	$.0904 \times 10^7$
18.8		158.9	$.0894 \times 10^7$
19.3		164.3	$.0900 \times 10^7$

IV. Retardation Readings with Flywheel.

Time, Seconds.	Speed, r. p. m.	Time, Seconds.	Speed, r. p. m.
0	1175	49.0	440
8.5	1030	63.2	294
16.9	882	78.0	147
26.7	735	93.8	0
37.2	588		

V. Total Stray Power Losses With Flywheel.

$$\frac{dn}{dt} = .2885.$$

n	$4\pi^2 I \cdot n \frac{dn}{dt}$	n	$4\pi^2 I \cdot n \frac{dn}{dt}$
17.1	144.1	18.6	157
17.4	147	18.8	159
17.8	150	19.1	161
18.1	152.8	19.3	163
18.3	154.5		

VI. Retardation Readings Without Flywheel.

Speed, r. p. m.	Time Seconds. (1)	(2)	(3)
1000	.1	.2	.2
900	.8	1.5	1.1
800	1.5	2.8	2.0
700	2.2	4.2	2.9
600	2.9	5.7	3.8
500	3.6	7.3	4.6
400	4.3	9.0	5.5
300	5.0	10.8	6.5
200	5.7	12.5	7.5
100	6.4	14.7	8.6
0	7.1	17.0	10.1

(1) Field excited, brushes on.
(2) Field unexcited, brushes on.
(3) Field excited, brushes off.

VII. Analysis of Losses Without Flywheel.

n Rev's per Second.	Total Stray Power.	Total Friction.	Core.	Bearing Friction + Core.	Bearing Friction.	Brush Friction.
17.1	144.7	77.2	67.5	114	46.5	30.7
17.4	147.2	78.5	68.7	116	47.3	31.2
17.8	150.7	80.3	70.4	118.5	48.1	32.2
18.1	153.2	81.6	71.6	120.6	49.0	32.6
18.3	154.9	82.6	72.4	122	49.6	32.9
18.6	157.3	83.9	73.4	124	50.6	33.3
18.8	159.1	84.8	74.3	125.6	51.0	33.8
19.1	161.5	86.6	74.9	128	52.1	34.3
19.3	163.4	87.0	76.4	128.5	52.1	34.9

(1) $\frac{dn}{dt} = 2.400$ (2) $\frac{dn}{dt} = 1.278$ (3) $\frac{dn}{dt} = 1.889$

VIII. Comparison of Results, Total Stray Power Loss.

n Rev's per Second.	Stray Power Method.	Retardation Method.	
		Flywheel off.	Flywheel on.
17.1	143.4	144.7	144.1
17.4	145.9	147.2	147
17.8	151.2	150.7	150
18.1	153.9	153.2	152.8
18.3	156.4	154.9	154.9
18.6	158.9	157.3	157
18.8	158.9	159.1	159
19.1	161.7	161.5	161
19.3	164.3	163.4	163

IX. Separation of Eddy-Current Losses.

Proceeding as in Par. 2, the point where the dn/dt curve tends to cut the axis of zero speed is about .82. $A = 4\pi^2 I\, dn/dt = 39.4 \times .0895 \times 10 \times .82$.

Hysteresis + Bearing Friction.	Hysteresis.	Eddy-Currents.
49.5	3.5	64.5
50.4	3.1	65.6
51.5	3.4	67.0
52.3	3.3	68.3
52.8	3.2	69.2
53.8	3.2	70.2
54.3	3.3	71.0
55.5	3.2	71.7
55.8	3.7	72.7

All losses in watts.

THE METHOD OF KEEPING "STOPE BOOKS" IN THE MINES OF THE BUTTE DISTRICT, MONTANA.

By CHARLES E. MORRISON, C.E.

In mining, as in any business enterprise, systematized records are essential to safeguard against error, and in no part of the work are they more important than in that which deals with the actual extraction of mineral.

Such records might be divided into those referring to the geological features alone, and those which relate to the general characteristics of the ore bodies as to size, location, mode of development, timbering, etc. The latter might again be divided into, first, data relating to work done in the levels, and, second, data relating to work done in the stopes. The former would naturally be gathered through the surveys, which would vary according to the amount of information found to be necessary for the office estimates, and to the desires of the engineer. It would be preserved through composite level maps indicating the relation of one sill to another, and by single level maps which would show more in detail the development of each sill floor.

The manner of collecting this information depends on severa, factors, and it is the object of this article to outline the simple and complete system adopted in the Butte district. As is well known the ore bodies there are of such size that square set timbers are used in all drifts and in the stopes above them. The problem confronting the engineer was to devise such a scheme, dependent upon the surveys and the system of timbering, that with not too much refinement an accurate record could be maintained showing all the details relating to the stopes. Formerly it was the custom, as outlined by Mr. Joseph Barrell, in his article on "Stope Books," in "The Coal and Metal Miner's Pocket Book," in combination with the surveys and timbering, to arrange the stope book with reference lines passing through the center of the shaft and perpendicular to the strike of the vein, but as this method proved to be somewhat unsatisfactory, it has been modified to such an extent that the data may now be collected with much greater ease and accuracy.

To demonstrate the relation existing between the surveys and

652 DRIFT EAST.

Station.	H. I.	Angle Turned.	Mag. Bearing.	Floor Elev.	F. S. Elev.	Horizontal Dist.	Remarks.
2372 B. S. 2371	—2.35	285°–27′ 210 –54	N. 89° E.	—6.8	+3.10	56′.0 60 .0	To station 2373 W. face center last cap. To center of face of drift.

651 DRIFT WEST.

2372 B. S. 2371	—2.35	105°–27′ 210 –54	S. 89° W.	—6.8	+2.75	35′.0	To station 2374 E. face center of cap.
2374 B. S. 2372	—1.73	172 –17 344 –34	S. 91 W.	—6.8	+1.95	29 .16	To station 2375 E. face center of cap.
2375 B. S. 2374	—2.40	201 –33 43 –06	W. 77 W.	—6.75	+2.13	23 .60 30 .00	To station 2376 E. face center of cap. To center face of drift.

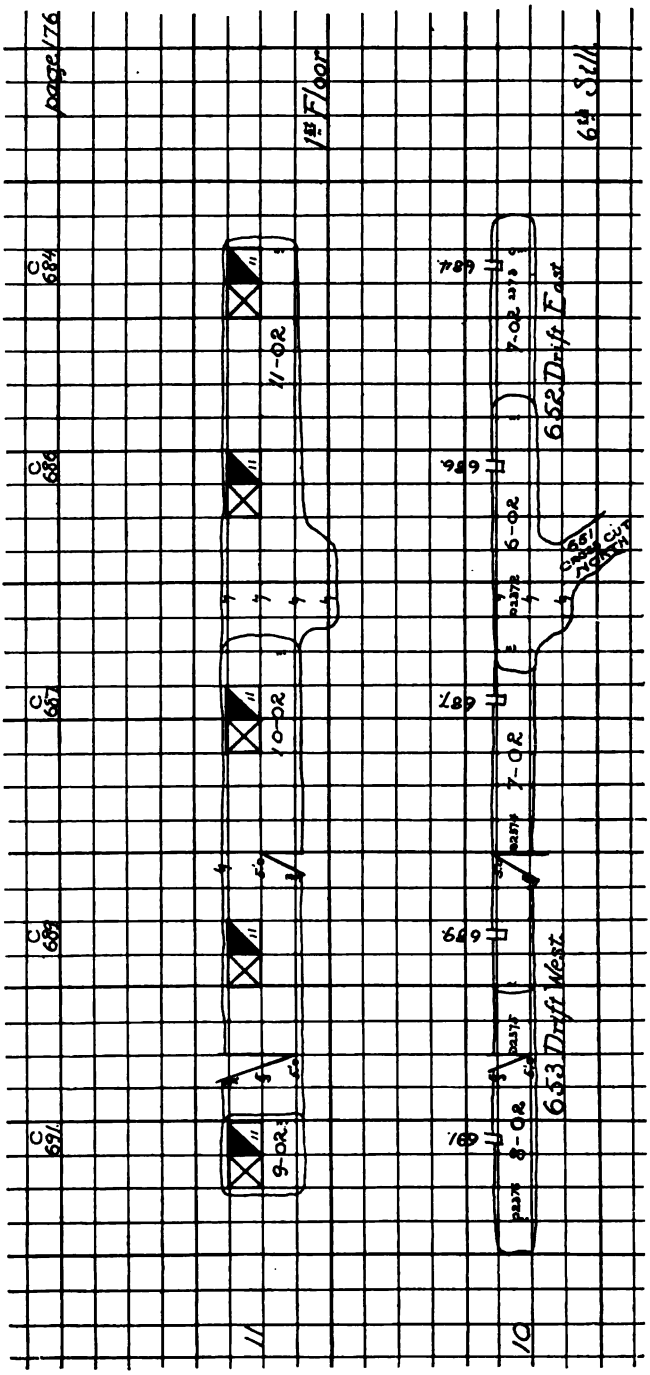

page 176
1st Floor
6th Sill
C 684
C 686
C 687
C 689
C 691
684
686
687
689
691
11-02
10-02
9-02
7-02
6-02
8-02
6-02 Drift East
6-03 Drift West
11
10

FIG. 1.

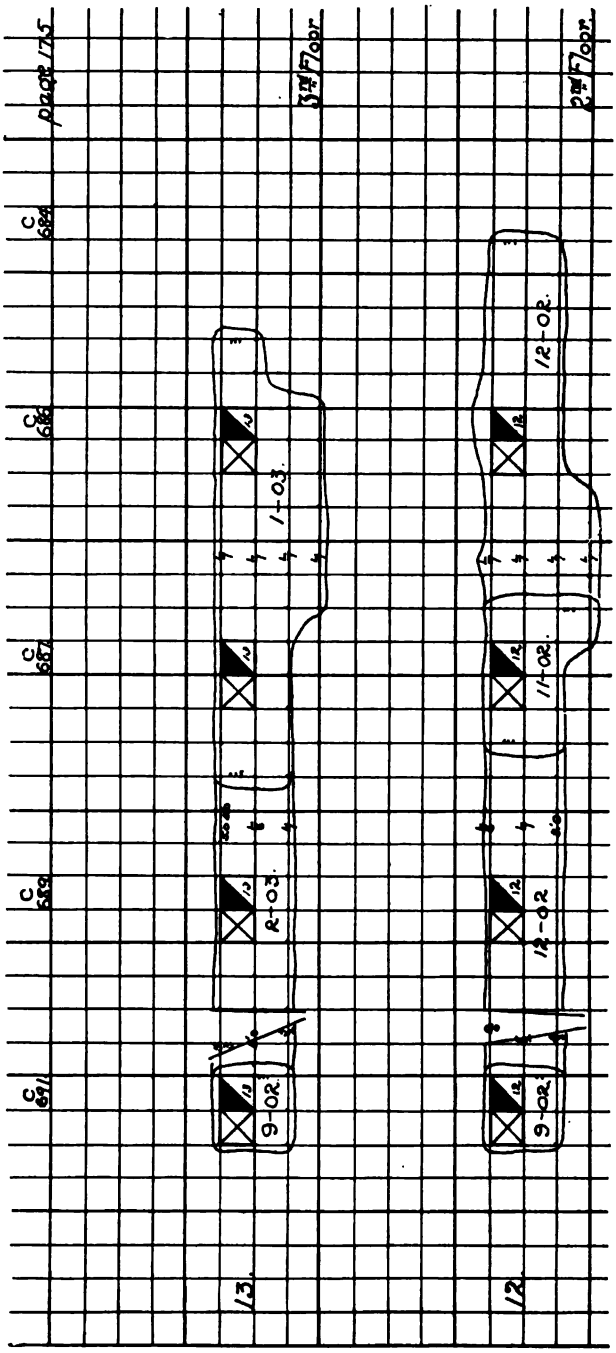

Floor 175
C 684
C 686
C 687
C 689
C 691
3rd Floor
2nd Floor
1-03.
2-03.
9-02.
12-02.
11-02.
12-02
9-02.
13.
12.

FIG. 2.

the stopes, it will be necessary to describe the former only in so far as they bear upon the latter.

Beginning at the shaft, the survey on every level is run out to the face of each cross-cut and drift as the work advances, being brought up to date once a month. Along the drifts, which are timbered with square sets, the points of the traverse are established on the caps, and wherever consistent the line of sight is made the center line of the drift. The angles are read in the usual manner, being doubled to avoid error, the magnetic bearing taken as a check, the elevation recorded and the horizontal distance measured. Notes and sketches (and this is very important) are made, showing the timbering angles, side sets, stations, manways and chutes with their numbers — in fact, every detail — so that it may be possible to plat in the office stope book an accurate plan map of the level with the timbers as they actually stand in the mine. Upon these notes and the map made from them, the rest of the work depends to a considerable degree. Such a set of notes is given below.

	Azimuth.	Bearing.	Distance.	Station.	Coördinates. N.	Coördinates. E.	Elevation.
2371	344°- 0′	N. 16° W.			3275.5	4576.4	5276.1
2372							
(2373)	285 -27	N. 89°-27′ E.	56′.0	(2373)	+.54	+56.0	+.75
	89 -27				3276.04	4632.4	5276.85
2371	344 - 0	N. 16 - 0 W.			3275.5	4576.4	5276.1
2372							
2374	105 -27	S. 89 -27 W.	35 .0	(2374)	-.34	-35.0	.40
	269 -27				3275.16	4541.4	5276.50
2375	172 -17	S. 81 -44 W.	29 .16	(2375)	-4.19	-28.86	.22
	261 -44				3270.97	4512.54	5276.72
2376	201 -33	N. 76 -43′ W.	23 .60	(2376)	+5.42	-22.97	-.27
	283 -17				3276.39	4489.57	5276.45

Assume that the coördinates of sta. 2372 (Fig. 1), are, N. 3275.5; E. 4576.4, and that the elevation is 5376.1, while the true bearing from sta. 2371 to sta. 2372 is N. 16°W. Upon this basis the following calculations, determining the coördinates and elevations of the successive stations, explain themselves. A traverse table is used to obtain the Northings and Eastings.

Between levels development work generally consists of raises or

winzes run from one sill floor to another, while the stoping of ore on each successive floor proceeds from these. Most frequently raises on narrow, almost vertical veins, are run from level to level, two sets wide along the lead and from "foot" to "hanging" (one set for the chute and the other for the manway).

Raise 691 is shown below in side elevation, and a plan of the 6th floor is given to indicate the position of the chute and manway.

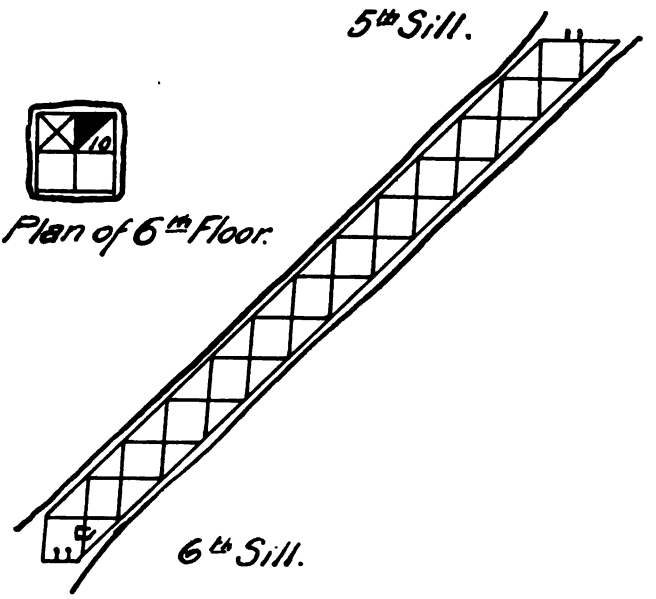


FIG. 3.

From the plan of the 6th floor it can be seen that the chute is to the right and the manway to the left, and that each occupies a foot-wall set, while the side elevation indicates that the raise offsets to the "foot" one set for each floor.

The field stope book is about ten and one-half inches long, by four and one-half inches wide, with stiff leather covers to prevent crushing and to protect it from the drippings of the mine waters. As a means of reference the back is labelled or stamped with the name of the mine, the vein or veins for which the book is a record and the numbers of the first and last pages. The body of the book consists of sheets of cross section paper of some convenient scale, each sheet being divided into squares of one inch by lines drawn heavier than the others, and every double page being numbered

consecutively. A scale of twenty feet to the inch has been found to give good results in this work, as it is large enough to permit of plenty of detail and not so large as to be cumbersome. Each square represents a square set, while a dot at the line intersections is used to indicate a post. With such a scale the book on being opened will represent on a double page, allowing for margins, about four hundred feet, in length, of the vein, and will be wide enough, where the veins are narrow, to permit of two floors being platted on the same sheet, one above the other.

To facilitate the work when in the mine the book is arranged in the office according to a system. Assuming a length of vein of four hundred feet and allowing two floors to a page, and a couple of pages to each level for a longitudinal section, cross sections of raises, winzes, and such other notes as are likely to need tabulation, the book is divided accordingly. Thus the first two double pages are reserved for the longitudinal section, etc., of level one, while page 3 will have the lower half reserved for the twelfth floor. Page 4 will contain floors 11 and 10, and so on down till we get to the first level, which will be on the lower half of page 9, with the first floor above it. The right hand edge of each page is marked for reference with the number of the floor opposite. On the ninth page where the level is, not only is the page marked, but a small leather tag with the number of the level is attached to the leaf, so that it protrudes beyond the edge. With the book closed, then, one can easily locate any level desired, after which it requires but the turning of a few pages to get the floor wanted. This is a great help in the mine when taking stopes, as it saves much time. In a similar manner, reservation would be made on the following pages for the data relating to the second level and the place for each floor would be indicated as in level one.

Where the vein is more than 400 feet long, this being the number of feet that can be platted on one double page, the book is divided into as many parts as there are 400-foot sections. If the length along the lead is between 400 and 800 feet, the book will be divided into two equal parts. The first half will contain a record of one section 400 feet long, from the top floor of the first level, through as many levels as the number of pages will permit; while the second half will contain a similar record of the other section of the vein. This arrangement readily shows the relation of levels, raises, winzes, etc., in any one section.

From actual platting in the mine, from the survey notes and from any other sources, the sketch of the sill floor of each level is made in the field book for the work of "taking up stopes" underground. In the case of 652 drift east and 653 drift west, Fig. 1, the field stope book platting would be identical with that in the survey book as shown. Too much care cannot be given in the preparation and platting of the stope book and too much detail can hardly be added, for any error in the sill floor will be carried up through the stopes, while lack of data may necessitate future trips to the mine where the conditions may be changed. Where the drift timbering is regular, that is, where each set conforms to the standard drift set for the mine, it is a simple matter to sketch in the posts of a set by a dot at each corner of a square. But many conditions arise where regular sets may not be used, and as the stope timbers above agree with the drift timbers or depend upon them for their correct platting, it is essential to indicate, since we cannot actually plat, just where and how each irregularity occurs.

Assume for demonstration that the drift is a straight one, except for a small bend, and that this bend can be overcome by a swing of two or three inches in one set, all the other sets being regular. The proposition would then be to indicate in preparing the field stope book, the position of this angle or bend with regard to the chutes, manways, stations, etc., on the sill floor, so that in showing the same bend in the stopes above, we will be assured of having it directly over that on the level. This is most important, since in a measure the relative position of chutes and bends is the means by which we quickly determine in the mine the correctness of the platting of the timbers in the stope book. Other irregularities arise, but these would be handled in a manner entirely similar to that which we shall use in explaining the method of "taking stopes" above Drifts 652 and 653. With the sill floor platted and the stope book prepared, we may enter the mine to collect the data which next follows in the record. This consists in the correct representations of all chutes and manways that have been run, on all floors, in such a manner that we shall know at a glance their true position with regard to the level and stope.

We will consider that raise 691 is the only one to have been begun before the stoping began, the others in the true sense being simply chutes and manways at the side and being run simultaneously with the stope. The side elevation of the raise shows that

it offsets one set to the foot wall for every floor gained in elevation. We will assume that the chute and manway is in every case in the footwall set as on floor six. If the drift set be given any arbitrary number, say 10, and for every offset to the foot we add one, then the chute and manway of 691 raise would be in row 11, on the first floor, in row 12 on the second, and so on up. The side elevation would give us a correct representation of the offsetting to the footwall, but from it we could not determine the offsetting to the east or west along the lead, should there be any. The plan of each floor furnishes this. Usually the chute goes directly to the next level without offsetting east or west along the lead, and in such a case the chute and manway would be platted on each sheet the same distance from the edge of the page. If it offsets one to the east it is platted one set to the right of the chute below, if to the west one set to the left.

Figs. 1 and 2 show the timbering of the sixth sill, 652 drift east and 653 drift west and the stoping above. Examining the sill floor sketch we learn from it that the work at the head of 651 cross-cut north was completed June, 1902 (6–02), that 652 drift east was finished in July, 1902, and that during July and August 652 drift west was brought to its present condition. It also shows that in the set where sta. 2372 is, the girts are 7′.0 center to center, that the rest of the timbering of the east drift is regular (5′.0 center to center of posts), that drift 653 has two bends in it, which way these bends turn and the position and number of the chutes.

Floor one shows that chute 691 is in the "foot," that the stope is two sets wide, one set being directly over the timbers in the drift, and the other to the "foot," the position of the bends and other chutes, and the date at which the work was prosecuted. The marks on the different caps are notches which are put in the timbers to indicate the timbering nearest to the face, and to help the surveyor taking stopes to locate himself when he next begins the work. The other floors show in a similar manner the details of the stope above.

Once a month this work is taken up by the surveyor, who in company with the shift boss visits all the stopes where ore has been mined.

The objects of the field stope book are many. It furnishes a permanent record of the work in the mine, shows the manner in which the development was prosecuted, the date at which it was

done, and supplies the data for office maps and estimates of amount of ore extracted, cost of same, and the possible ore reserve. From it the office stope book, which represents each ore body in its true relative position, is posted once a month; and through the information which it supplies a longitudinal section is made every six months and semi-annual estimates of ore reserve are furnished. In short, it shows the shape, location, and manner of development of any stope at any time.

NOTES ON ORGANIC ANALYSIS. PART II.

By Henry C. Sherman.

CHAPTER IV.

Aldehydes.

The most important methods for the detection and determination of aldehydes are based upon reactions of oxidation, of condensation and of direct addition.

The readiness with which aldehydes undergo oxidation, gives them the property of reducing ammoniacal silver solution which is the basis of one of the most delicate qualitative tests for this group of compounds. The test may be carried out as follows: *

Mix, in a test-tube previously cleaned with hot sodium hydroxide solution, 1 c. c. of ammoniacal silver nitrate solution (containing one part of silver nitrate in ten parts of ammonium hydroxide of 0.923 sp. gr.) and 1 c.c. of ten per cent. sodium hydroxide solution. Shake the mixture in the tube and then allow two or three drops of the solution to be tested to flow slowly down the moistened glass surface into the reagent. Shake and allow to stand cold for five minutes. Aldehydes (and a few other compounds including some of the polyatomic alcohols) cause the production of a dark brown or black precipitate or mirror of metallic silver. This reaction is given by all of the ordinary aldehydes of the fatty series, including the aldose carbohydrates, but not by all aromatic aldehydes.

The ammoniacal silver solution and the sodium hydroxide must not be mixed in advance and must always be kept cool as a dangerously explosive precipitate is apt to form on warming or on long standing. The use of a mixture of sodium hydroxide and ammoniacal silver nitrate (Tollens' aldehyde reagent) makes the test more delicate than when the ammoniacal silver solution is used alone.

Alkaline solutions of other metals are reduced by many aldehydes, especially on boiling, and many quantitative methods for in-

* Noyes and Mulliken: Identification and Class Reactions of Organic Substances. Mulliken: Identification of Pure Organic Compounds, Vol. I., p. 22.

dividual aldehydes are based upon the determination of the amount of metal reduced.

Condensation reactions, especially with phenylhydrazine, hydroxylamine and phenols are often used for the detection and sometimes for the determination of aldehydes. A general discussion of such methods will be found in the works of Vaubel* and of Meyer.† Several special methods will be described in this and the two following chapters.

Of the addition reactions of aldehydes, that with bisulphite is of especially wide application. On shaking a liquid aldehyde or a concentrated solution of aldehyde in water or ether, with an equal volume of strong sodium bisulphite solution, addition takes place with the formation of the saturated compound $RCH(OH)SO_3Na$ which usually separates as a white crystalline precipitate. Ketones containing the CH_3CO group also give the reaction. A negative result is not conclusive as the addition product may be too soluble to appear as a precipitate.

According to Ripper,‡ the bisulphite reaction can be utilized for the determination of any aldehyde soluble in water or which can be brought into solution by a small amount of alcohol. A one-half per cent. solution of the aldehyde is mixed with twice its volume of a solution of potassium bisulphite of known strength (about 12 grams per liter), and after 15 minutes the excess of bisulphite is determined by titration with iodine. Ripper applied this method with satisfactory results to solutions of formaldehyde, acetaldehyde, benzaldehyde and vanillin.

A similar addition reaction gives rise to the well-known and delicate "fuchsin test" for aldehydes. This test, as developed by Mulliken,§ is as follows:

To prepare the fuchsin aldehyde reagent, dissolve 0.2 gram of rosanilin, or, if the free base cannot be obtained, of the hydrochloride or acetate in 10 c.c. of a freshly prepared, cold, saturated aqueous solution of sulphur dioxide. Allow the solution to stand until all signs of pink disappear and it becomes colorless or pale yellow. This will require several hours. Then dilute with water to 200 c.c. and preserve for use in a tightly-stoppered bottle.

* Bestimmung organische Verbindungen.

† Analyse und Konstitutionsermittlung organischer Verbindungen.

‡ *Monatsh. Chem.*, 1900, 21, 1079.

§ Identification of Pure Organic Compounds, Vol. I, p. 15.

To 5 c.c. of this reagent add 0.05 gram, or one drop, of the substance to be tested (if pure, or a few drops if in solution). If the substance is a liquid, or dissolves in the reagent, allow to stand two minutes and observe the color. If the substance does not dissolve, shake gently for two minutes and then observe the color. The appearance of a distinct pink, red, purple or blue coloration indicates the presence of an aldehyde. The test to be of value must be applied under carefully regulated conditions. The reagent is reddened by alkalies or alkaline salts of weak acids, by heating or by long exposure to air at ordinary temperature. In general, the test as here described distinguishes aldehydes other than carbohydrates from the latter and from ketones. A few acetals show the reaction through being partially hydrolyzed to aldehydes under the conditions of the test. Acetone and some other soluble ketones prepared by destructive distillation gradually redden the reagent if added to it in large quantity or if allowed to remain in contact for a number of minutes; but this is thought to be due chiefly, if not wholly, to the presence of traces of aldehydes or acetals (Mulliken).

This reaction serves for the detection of minute quantities of aldehydes present as impurities in commercial alcohol, and for the colorimetric estimation of aldehydes in distilled liquors.*

FORMALDEHYDE.

Formaldehyde gas, produced by the partial oxidation of methyl alcohol, is freely soluble in water and is most commonly handled as a 35 to 40 per cent. aqueous solution. Such solutions are often designated formalin, formol or formal. More dilute solutions are extensively sold as food preservatives, often under fanciful or misleading names.

In dilute aqueous solution, formaldehyde exists in the "monomolecular" state, as CH_2O. Such solutions do not change if kept at ordinary temperature in closed vessels. When an aqueous solution is concentrated either by spontaneous evaporation or by heating, a white flocculent deposit appears. If the solution is then separated from the deposit it is found to contain condensed or polymerized formaldehyde.† The material which deposits from

*Medicus: *Forschungsber. über Lebensmittel*, 1895, 1, 299; Bulls. 46 and 65, Bur. Chem., U. S. Dept. Agriculture.

† Tollens and Mayer: *Ber. deut. chem. Ges.*, 1888, 21, 1571, 3503. Kraut, Eschweiler and Grossmann: *Ann. Chem.*, 1890, 258, 103.

a concentrated aqueous solution of formaldehyde has, after drying, the composition $(CH_2O)_6 \cdot H_2O$ to $(CH_2O)_8 \cdot H_2O$.* It is amorphous, soluble in warm water and has an odor resembling that of formaldehyde. The paraformaldehyde of commerce consists essentially of this material.

Metaformaldehyde (oxymethylene, "trioxymethylene"), $(CH_2O)_x$, may also be formed by evaporation of formaldehyde solutions. By prolonged digestion at ordinary temperature or by heating for a short time at 130°–150° with a large excess of water, metaformaldehyde passes into solution and into the "mono-molecular" form. Polymeric modifications of formaldehyde in aqueous solution resemble closely the original substance in its behavior toward reagents so that, as measured by the ordinary methods, a solution does not lose strength by the partial polymerization of the formaldehyde so long as all remains in solution.

Commercial solutions of formaldehyde commonly contain methyl alcohol and may contain any of the impurities of commercial wood spirit. Solutions of the usual strength, 35 to 40 per cent., should have specific gravities of about 1.08 to 1.11 at 15°, lower figures ordinarily indicating the presence of excessive amounts of methyl alcohol.†

The methods given in this chapter for the detection and determination of formaldehyde refer especially to the examination of commercial solutions containing only such impurities as ordinarily occur in crude preparations of formaldehyde, or substances which might be used with formaldehyde in preservative mixtures. The examination of food products for formaldehyde will be discussed in connection with other food preservatives in a subsequent chapter.

If a solution to be examined contains dissolved solids which interfere with the direct application of the tests as described, it can be acidified with a small excess of phosphoric or sulphuric acid, distilled, and the test applied to the distillate. The latter, however, will never contain all of the formaldehyde, since some is always polymerized and left as paraformaldehyde in the distilling flask.

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* Lösekann: *Chem. Ztg.*, 1890, 14, 1408. Delephine: *Compt. rend.*, 1897, 124, 1525; Beilstein: *Organische Chemie*, Erganzbd., I., 467.

† On the determination of methyl alcohol in formaldehyde solutions see—Duyk: *Ann. Chim. Anal. Appl.*, 1901, 6, 407; *Journ. Chem. Soc.*, 1902, 82, ii, 110. Stritrar: *Ztschr. anal. Chem.*, 1904, 43, 401. Gnehm and Kaufler: *Ztschr. angew. Chem.*, 1904, 17, 673. Bamberger: *Ibid.*, 1904, 17, 1246.

Detection and Identification.

*Resorcin Test.**

Mix one drop of a 1 per cent. aqueous solution of resorcin with 1 c.c. of a dilute aqueous solution (preferably about 0.2 per cent.) of the aldehyde. Allow the mixture to flow gently down the side of an inclined test-tube containing 3–5 c.c. of pure concentrated sulphuric acid (or incline the test-tube containing the mixture and pour in the acid). Impart a gentle rotary motion to the liquids by cautiously swaying the lower end of the tube through a circle about a decimeter in diameter, in such a manner as not to cause the disappearance of the two layers. If formaldehyde is present, a red ring slightly tinged with violet will soon appear. Above this ring a light flocculent precipitate, at first nearly white on its upper surface and red-violet beneath, but soon changing to flocks that are red throughout, will be seen suspended in the aqueous upper layer.

This reaction is very satisfactory for solutions containing one part of formaldehyde in 100 to 5000 parts of solution and can be detected to a dilution of 1 : 100,000. A similar reaction is obtained if phenol is used instead of resorcin.

Gallic Acid Test. †

Mix 0.2 c.c. of a saturated solution of gallic acid in pure ethyl alcohol, with 1 to 2 c.c. of the solution to be tested and introduce a layer of concentrated sulphuric acid, as in the resorcin test. In the presence of formaldehyde, a green zone appears at the line of contact of the two liquids. This gradually changes to a pure blue ring, which, in the case of pure aqueous solutions of formaldehyde, can be detected without difficulty at a dilution of 1 : 500,000. If the solution tested contains as much as one part of formaldehyde in 20,000, a yellowish color appears immediately at the line of contact of the two liquids. This quickly turns green, and the blue color develops both above and below the green zone. If other substances which give color reactions are also present, the upper layer will vary in color, but the green and lower blue ring will still appear beneath

* Mulliken and Scudder: *Amer. Chem. Journ.*, 1900, 24, 451. Mulliken: Identification of Pure Organic Compounds, Vol. I, p. 24.

† Barbier and Jandrier: *Ann. Chem. Anal. Appl.*, 1, 325; Abs. *Analyst*, 1896, 21, 295. Mulliken and Scudder: *Amer. Chem. Journ.*, 1900, 24, 446.

(Mulliken and Scudder). On swaying the tube, or allowing it to stand for some time, the blue color spreads throughout the zone and a pure blue ring is usually obtained. The color is quite permanent and apparently quite characteristic, no other substance having been noted as giving the blue ring. Acetaldehyde tested in the same way gives a reddish brown coloration.

Hydrochloric Acid and Casein Test. *

Mix 5 c.c. of the solution to be tested with 5 c.c. of pure milk in a porcelain casserole, add 10 c.c. of concentrated hydrochloric acid containing 0.002 gram of ferric chloride and heat slowly over a free flame nearly to boiling, meanwhile giving the casserole a rotary motion to break up the curd. A violet coloration indicates formaldehyde. According to Leach, various aldehydes give color reactions under this treatment, but formaldehyde alone shows the unmistakable, violet coloration. This test is especially useful for the detection of formaldehyde in food, and will be more fully discussed in connection with the detection of food preservatives

Methylene-di-β-naphthol Test.

Since formaldehyde is frequently sold under other names, its identification by some method independent of the above color reactions may be a matter of importance. In such cases the following test given by Mulliken † will be useful.

Place in a test-tube 3 drops of a 30 to 40 per cent., or 10 drops of a 10 per cent. solution, 3 c.c. of dilute alcohol (1 : 2), 0.04 to 0.06 gram β-naphthol, and 3 to 5 drops of concentrated hydrochloric acid. Boil gently until the liquid becomes filled with an abundant precipitate of small white needles. Filter while hot. Wash with 1 c.c. of dilute alcohol (1 : 2). Boil the precipitate with 4 c.c. of dilute alco-hol (1 : 1.) (It is not necessary that all should dissolve.) Cool and filter off the precipitate. Wash with 1 c.c. of dilute alcohol (1 : 1.) Dry on porous tile in a warm place and determine the melting point.

Methylene-di-β-naphthol, the product, forms white needles, which, when the temperature in the neighborhood of the melting point is raised at the rate of 1° in 15 seconds, begin to turn brown

* Leach : Ann. Rept. Mass. State Board of Health 1897, 558; 1899, 699. Food Inspection and Control (New York, 1904), p. 140.

† Identification of Pure Organic Compounds, Vol. I., p 24.

at 180°. It melts with decomposition to a red-brown liquid at 189°–192° (uncor.).

Determination by Oxidation.

Iodimetric Method. *

This method depends upon the oxidation of formaldehyde to formic acid by means of iodine in alkaline solution. Two atoms of iodine oxidize one molecule of formaldehyde and the excess of iodine is liberated by acidulation and determined by titration with sodium thiosulphate.

Reagents. — Standard solutions of iodine and sodium thiosulphate, preferably about tenth-normal. Approximately normal solutions of sodium hydroxide and hydrochloric acid.

Determination. — Dilute a weighed portion of the sample with a known quantity of water so as to obtain a solution containing 0.5 to 1 per cent. of actual formaldehyde. Mix 10 c.c. of this solution with 25 c.c. normal sodium hydroxide and add from a burette 50 to 75 c.c. of tenth-normal iodine solution or enough to assure an excess of iodine as shown by the permanent yellow color of the solution. Shake or stir thoroughly and after ten minutes add 35 c.c. normal hydrochloric acid and titrate with sodium thiosulphate in the usual way using starch solution as indicator. At the same time determine the strength of the iodine in terms of the thiosulphate solution and from the amount of iodine consumed in oxidizing the formaldehyde, calculate the weight of the latter in the ten c.c. taken for the determination.

Notes. — Under the conditions given the oxidation of formaldehyde is rapid and complete but the method is applicable only in the absence of all other substances capable of consuming iodine under these conditions. Other aldehydes, acetone and alcohol cause high results, the latter probably through absorbing iodine with the formation of chloroform.

In the absence of interfering compounds, the method is very satisfactory, even for solutions containing only one-tenth per cent. of formaldehyde. Variations in the excess of iodine added have no appreciable influence upon the results.

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* Romijn: *Ztschr. anal. Chem.*, 1897, 36, 18. Williams: Essay for the Degree of Master of Arts, Columbia University, November 1904.

*Hydrogen Peroxide Method.**

In this method, formaldehyde is oxidized to formic acid by means of hydrogen peroxide in the presence of a known amount of alkali. The excess of alkali, over that required to combine with the formic acid produced, is determined by titration.

Reagents. — Standard solutions of sodium hydroxide and sulphuric acid, not weaker than normal nor stronger than twice normal. Neutral † 3 per cent. solution of hydrogen peroxide. Litmus solution as indicator.

Determination. — Weigh 2 to 3 grams of the solution to be tested in a stoppered flask or bottle, add 30 to 50 c.c. normal sodium hydroxide and then add cautiously from a pipette, 50 c.c. of the peroxide solution, insert the stopper loosely and allow to stand at room temperature, shaking frequently until evolution of gas ceases. Working in a warm room with double normal alkali and with samples containing over 30 per cent. of formaldehyde the reaction takes place readily with considerable production of heat, and is complete within ten minutes. If normal alkali is used and the work is done in a cold room or with a more dilute solution of formaldehyde, an hour should be allowed for the oxidation of the formaldehyde by the peroxide. Finally add a few drops of litmus solution and titrate the alkali remaining uncombined. Each molecule of sodium hydroxide which has been consumed (deducting the amount required to neutralize any free acid which the peroxide solution or the original solution of formaldehyde may have contained) represents one molecule of formaldehyde oxidized to formic acid.

Notes. — For the best results the strength of alkali and the time allowed for the reaction should be governed by the concentration of the formaldehyde solution tested. Double normal alkali is usually recommended and the reaction is said to be complete in ten minutes with solutions containing as little as 5 per cent. of formaldehyde. For stronger solutions the method is made more accurate by using normal or sesqui-normal alkali and allowing an hour for the oxidation.

Acetaldehyde is partially oxidized under the same conditions. Its presence, therefore, causes high results but not so high as by

* Blank and Finkenbeiner: *Ber. deut. chem. Ges.*, 1898, 31, 2979.

† If all available peroxide is acid, the acidity must be determined by titration, using litmus as indicator, and allowed for in calculating the amount of alkali consumed in the formaldehyde determination.

the iodimetric method. The results are not influenced by the presence of paraldehyde, acetone or ethyl or methyl alcohol. Commercial formalin containing only traces of acetone or acetaldehyde should show the same percentage of formaldehyde by the peroxide as by the iodimetric method.

Determination by Condensation Reactions.

Several of the condensation reactions of formaldehyde have been utilized for its quantitative determination. One of the oldest and best-known methods is based upon the fact that formaldehyde and ammonia when mixed in not too dilute solution condense to form hexamethylene tetramine:

$$6CH_2O + 4NH_4OH = N_4(CH_2)_6 + 10H_2O.$$

If a known amount of ammonia is used, the determination of the excess shows the amount of formaldehyde originally present.

*Legler's Ammonia Method.**

Weigh about 1.5 grams of the solution containing 30 to 40 per cent. formaldehyde, or an equivalent amount of a more dilute solution, into a 250 c.c. glass-stoppered flask or bottle. Add 100 c.c. of fifth-normal ammonia solution; stopper tightly at once; mix and allow to stand over night at room temperature. Standing for two or three days does no harm, provided the stopper fits so tightly as to prevent any loss of ammonia. Finally, add a very small amount of rosalic acid as indicator and titrate the excess of ammonia with standard sulphuric acid. Calculate the quantity of formaldehyde originally present from the amount of ammonia consumed in condensing with it according to the equation given above.

Notes and Precautions. — In order to prevent loss of ammonia during the determination, the flask or bottle must be very tightly closed, the stopper being coated with vaseline if necessary. For the same reason the excess of ammonia should be titrated quickly after opening the flask. Normal or half-normal ammonia is commonly recommended for this method, but the fifth-normal solution is less likely to lose strength and has been found by Williams to give as complete reactions as the stronger solutions. In titrating

* Legler: *Ber. deut. chem. Ges.*, 1883, 16, 1333. Smith: *Journ. Amer. Chem. Soc.*, 1903, 25, 1028. Williams: *loc. cit.*

the excess of ammonia the end reaction is usually unsatisfactory, especially when the solution is highly colored by the indicator. Two drops of a freshly prepared 0.1 per cent. solution of rosalic acid has been found sufficient. With a view to obtaining a sharper end reaction, Williams recommended diluting the commercial formalin so as to obtain a solution containing about 2 per cent. of formaldehyde. Mix 10 c.c. of this solution with 40 c.c. of fifth-normal ammonia in a small glass-stoppered bottle and complete the determination as above described. The method is thus applicable to solutions containing only 1 to 2 per cent. of formaldehyde, although its results in such cases may be somewhat low.

The results are not affected by the presence of acetone, methyl or ethyl alcohol, paraldehyde or benzaldehyde. Acetaldehyde reacts with ammonia and thus causes high results if present in the formaldehyde solution.

This method, carefully carried out as described, gives results lower than those obtained by the peroxide method. The discrepancy varies greatly with different analysts and appears to be largely dependent upon the interpretation of the end-point in titrating the excess of ammonia. The color change is not sharp, but by using very little indicator a fairly definite point can be noted at which the pink tint disappears, leaving the solution nearly colorless. This is the most distinct and satisfactory end-point. It has been suggested, however, that the indistinctness of the end reaction may be due to the faintly basic character of the hexamethylenetetramine, and that the first indication of a color change should be taken as showing the point at which the excess of ammonia is neutralized. This mode of titration yields higher results which often agree with those obtained by oxidation methods. As yet there is no standard by which to judge whether the higher or the lower results are more nearly correct.

Determination by Addition Reactions.

The general addition reaction of aldehydes with bisulphites has been used quantitatively by Ripper, as already noted. For the determination of formaldehyde, however, the reaction with potassium cyanide has been found especially useful.

*Potassium Cyanide Method.**

On mixing aqueous solutions of formaldehyde and potassium

* Romijn: *Ztschr. anal. Chem.*, 1897, 36, 18. Smith: *loc. cit.* Williams: *loc. cit.*

cyanide an addition product is formed, which, according to Romijn, is probably the potassium compound of oxyacetonitril:

$$CH_2O + KCN = CH_2OK{\cdot}CN.$$

The addition product reduces silver nitrate in alkaline solution, but has no effect in the presence of an excess of nitric acid. If, therefore, the formaldehyde to be tested be mixed with a known solution of potassium cyanide, the latter being in excess, and the mixture added to a standard solution of silver nitrate acidulated with nitric acid, only the excess of potassium cyanide reacts with the silver nitrate. The amount of formaldehyde originally present is shown by the quantity of potassium cyanide consumed in the formation of the addition product. The details of the method as here given are nearly identical with those originally recommended by Romijn.

Reagents. — Tenth normal solutions of silver nitrate and ammonium thiocyanate. A solution of potassium cyanide 6.2 grams per liter. Saturated solution of ferric ammonium sulphate. Nitric acid 1.32 sp. gr. (fifty per cent.).

Determination.—(1) Measure 15 c.c. tenth-normal silver nitrate into a 100 c.c. flask, add 6 to 8 drops of the nitric acid and 10 c.c. of the cyanide solution; shake, dilute to the mark, mix thoroughly and filter through a dry paper. Titrate 50 c.c. of the filtrate with tenth-normal ammonium thiocyanate, using 5 c.c. of the ferric solution as indicator. The strength of the silver and of the thiocyanate solutions being known, this titration shows the strength of the cyanide.

(2) Dilute the sample until it contains about 1 per cent. of formaldehyde, mix 10 c.c. of this dilute solution with 35 c.c. of the cyanide solution and rinse the mixture into another portion of 15 c.c. tenth-normal silver nitrate, acidulated with 6 to 8 drops of the nitric acid and contained in a 100 c.c. flask; shake and determine the excess of silver by means of thiocyanate in the same way as before. Twice the difference between the two titrations (since only half the liquid was used in each case) represents the amount of cyanide consumed by the formaldehyde. If the thiocyanate solution is exactly tenth-normal, twice the difference (in c.c.) between the two titrations, multiplied by 0.003002, gives the weight of formaldehyde (in grams) in the portion taken for the determination.

Notes.—This method is applicable to very dilute solutions of formaldehyde, larger volumes being used in place of the 10 c.c. called for in the above directions. Smith obtained accurate results upon a solution containing 0.01 per cent.

Ethyl and methyl alcohols, acetone, benzaldehyde and paraldehyde do not interfere. Acetaldehyde causes high results if allowed to stand for some time in contact with the cyanide solution, but if the formaldehyde solution is added to the cyanide and, after mixing, poured at once into the silver nitrate solution, the presence of acetaldehyde does not influence the results. With commercially pure solutions of formaldehyde in water Romijn and Smith obtained concordant results by the iodimetric and cyanide methods. Williams obtained concordant results by the ammonia and the cyanide methods which were lower than those obtained by the oxidation methods.

Additional References.

(These papers deal with the determination of formaldehyde. Additional qualitative tests will be under food preservatives in a later chapter.)

Trillat: *Bull. Soc. Chim.*, 1893, [3], 9, 305.
Brochet and Cambier: *Compt. rend.*, 1895, 120, 449, 557.
H. M. Smith: *Analyst*, 1896, 21, 148.
Grützner: *Arch. Pharm.*, 1896, 234, 634; Abs. *Ztschr. anal. Chem.*, 1897, 36, 527.
Orchard: *Analyst*, 1897, 22, 4.
C. E. Smith: *Amer. Jour. Pharm.*, 1898, 70, 86.
Kehler: *Ibid.*, 1898, 70, 432.
Tollens and Clowes: *Ber. deut. chem. Ges.*, 1899, 32, 2841.
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Vanino: *Ibid.* 1901, 40, 720.
Craig: *Journ. Amer. Chem. Soc.*, 1901, 23, 638.
Peska: *Chem. Ztg.*, 1901, 25, 743.
Pfaff: *Ibid.*, 1902, 26, 701.
Schiff: *Ibid.*, 1903, 27, 14.
Lemme: *Ibid.*, 1903, 27, 896.
Wallnitz: *Gerberztg.*, 1903; Abs. *Analyst*, 1903, 28, 189.

CHAPTER V.

Carbohydrates — General Methods.

The carbohydrates include the simple sugars (monosaccharides) and the substances which can be converted into simple sugars by hydrolysis. The monosaccharides are aldehyde alcohols or ketone alcohols, each molecule containing a carbonyl group and several hydroxyl groups, one of the latter being adjacent to the carbonyl group (Meyer-Jacobson).

The purpose of this chapter is to outline the more important analytical properties of the following carbohydrates:

Monosaccharides: Hexoses — Dextrose (d. glucose), Levulose (d. fructose), Galactose, Mannose; Pentoses — Xylose, Arabinose.

Disaccharides: Sucrose, Lactose, Maltose.

Trisaccharide: Raffinose.

Polysaccharides: Starch, Dextrin, Glycogen, Galactan, Cellulose, Pentosans.

In addition to a few notes on the occurrence, relations and solubilities of these carbohydrates, their reactions with phenylhydrazine and with alkaline copper solutions, their behavior on treatment with acids and their power of rotating the plane of polarized light will be considered.

OCCURRENCE AND RELATIONS.

Monosaccharides (glucoses, glycoses, monoses) have the composition $(CH_2O)_x$* and are called tetroses, pentoses, hexoses, etc., according to the number of carbon atoms in the molecule. Only pentoses and hexoses are of sufficient practical importance to call for consideration in connection with ordinary methods of analysis. The pentoses do not occur free in nature but are met by the analyst as products of the hydrolysis of the pentosans. The hexoses include all of the monosaccharides of present commercial importance and all whose biological relations have been thoroughly studied.

Dextrose (d. glucose, grape sugar, starch sugar, diabetic sugar, ordinary glucose) is widely distributed in nature, occurring especially in fruits and plant juices, often mixed with other sugars. It is a

* This statement does not apply to the methyl derivates now frequently classified as monosaccharides.

normal constituent of blood and is the form of carbohydrate ordinarily found in the urine in diabetes or glycosuria. With the exception of the pentosans and galactan all of the di-, tri-, and polysaccharides mentioned above yield dextrose on hydrolysis.

Levulose (d. fructose, fruit sugar) occurs with dextrose in plant juices and especially in fruits and honey. It is also a product of the hydrolysis of sucrose and of raffinose.

Galactose does not occur free but as a product of hydrolysis of lactose, raffinose and the galactans it is of considerable analytical importance.

Mannose also is not found free but has been detected among the products of hydrolysis of the insoluble carbohydrate matter of a number of thick-walled vegetable tissues, nut shells, etc., and of several Japanese vegetables.

The disaccharides considered here are all hexo-bioses ($C_{12}H_{22}O_{11}$).

Sucrose (saccharose, cane sugar) is widely distributed in the vegetable kingdom being found in considerable quantity, generally mixed with dextrose and levulose, in the fruits and juices of many plants. The most important sources of sucrose are the sugar beet, the sugar and sorghum canes, and the sugar maple. A molecule of sucrose yields on hydrolysis one molecule each of dextrose and levulose. The hydrolysis of sucrose is often called "inversion" and the resulting mixture of equal parts dextrose and levulose is known as "invert sugar."

Lactose (lactobiose, milk sugar) occurs in the milk of most mammals, constituting usually from 4 to 7 per cent. of the fresh secretion. Lactose crystallizes with one molecule of water which it retains on drying at room temperature over sulphuric acid or on heating in the air at 100°, but loses at about 130°. A molecule of lactose yields on hydrolysis one molecule each of dextrose and galactose.

Maltose (malt sugar) is formed from starch by the action of diastatic enzymes and is therefore an important constituent of germinating cereals, malt, malt extract and beer wort. It is also formed as an intermediate product when starch is hydrolyzed to dextrose by boiling with dilute mineral acids, as in the manufacture of commercial glucose. Maltose crystallizes with one molecule of water which it loses on heating in the air at 100°. Each molecule of maltose yields two molecules of dextrose on hydrolysis.

The only trisaccharide of practical importance is raffinose

($C_{18}H_{32}O_{16}$) also called meletriose and formerly melitose or gossypose. It occurs in cotton seed and in small quantity in the germs of various other seeds including wheat and barley. Sugar beets, especially if unhealthy or injured, sometimes contain raffinose in sufficient quantity to affect the refining process. Raffinose crystallizes with five molecules of water in needles or slender prisms and has a marked influence upon the crystallization of the cane sugar present. * Raffinose loses its water of crystallization at 100°. On hydrolysis it yields one molecule each of dextose, levulose and galactose. Partial hydrolysis results in the formation of levulose and the disaccharide, melibiose.

Starch $(C_6H_{10}O_5)_x$ is the most important of the polysaccharides being the principal form of carbohydrate in grains, and most other edible seeds, as well as in potatoes and other tubers. It is the main product of the assimilation process and the principal reserve carbohydrate of most green plants. Commercially it is of great importance as a constituent of foods, as the source of dextrin, maltose and commercial glucose and as the principal raw material of many of the fermentation industries. Starch constitutes over one-half of the solid matter of all ordinary cereals and about three-fourths of the total solids in potatoes. Starch granules of different plants vary in size and structure so that in most cases the source of a starch which has not been altered by heat, ferments or chemical reagents, can be determined by microscopical examination. All starches yield dextose only, as the final product of complete hydrolysis.

Dextrins, $(C_6H_{10}O_5)_x$ or $(C_6H_{10}O_5)_x \cdot H_2O$, are formed from starch by the action of enzymes, acids or heat. Small amounts of dextrin are found in normal, and larger amounts in germinating, cereals. Malt diastase acting upon starch in fairly concentrated solution yields usually about one part of dextrin to four of maltose. During acid hydrolysis, dextrin is formed as an intermediate product between soluble starch and maltose. Commercial dextrin, the principal constituent of "British gum," is obtained by heating starch, either alone or with a small amount of dilute acid.

Glycogen, $(C_6H_{10}O_5)_x$ or perhaps $(C_6H_{10}O_5)_x \cdot H_2O$, is the principal carbohydrate of the animal organism being found in small quantity in the muscles and more abundantly in the liver of all well-nourished animals. It is a white amorphous powder intermediate

* Stone and Baird: *Journ. Amer. Chem. Soc.*, 1897, 19, 116.

in properties between starch and dextrin and is sometimes called animal starch. The determination of glycogen is often important in physiological investigations and is sometimes useful in distinguishing horseflesh from beef, the latter containing usually less than 0.7 per cent. of glycogen, the former often two or three times this amount. On complete hydrolysis glycogen yields only dextrose.

Galactans, amorphous polysaccharides yielding galactose on hydrolysis, occur in small quantity in many plants and in relatively large amount in the seeds of the legumes where they largely replace starch as reserve carbohydrate. Since the galactans are readily hydrolyzed by hot dilute acids and are digested by some of the diastatic enzymes, it is probable that galactan has been reported as starch in many analyses.

Cellulose occurs in the cell walls of all vegetable tissues. The term is sometimes applied to the whole of the fiber which is unattacked by boiling dilute acids and alkalies but should be restricted to that constituent of the fiber which is of a true carbohydrate nature. "Normal" cellulose, such as is derived from cotton and flax fibers, yields dextrose on hydrolysis. A few celluloses have been found to yield mannose or a pentose (probably xylose) in addition to dextrose (Tollens).

Pentosans, anhydrides of arabinose and xylose, are the principal constituents of the vegetable gums, araban occurring especially in the soluble gums such as cherry gum and gum arabic, xylan in the so-called woodgum of fibrous tissues, such as wood, straw, vegetables, and the outer portion of the cereal grains. The wheat grain, for example, contains 3 to 5 per cent. of pentosan which in the milling process is largely left in the bran. The so-called patent flour obtained from the interior of the grain contains hardly any pentosan while the breakfast cereals and the so-called entire wheat and graham flours have usually about as much as the original grain.

SOLUBILITIES.

In Water.

Of the carbohydrates mentioned above, all except the polysaccharides are crystallizable compounds dissolving in water to form clear solutions. Milk sugar dissolves in six parts of water at ordinary temperature; all of the other members are more freely solu-

ble. Among the polysaccharides dextrin, glycogen and some of the galactans and pentosans are soluble; starch, cellulose, some of the galactans and most of the pentosans of ordinary food materials are insoluble in cold water. Glycogen gives a strongly opalescent solution, which is not cleared by repeated filtration but loses its opalesence on the addition of a little potassium hydroxide or acetic acid. On heating with water, starch grains swell and finally gelatinize with the formation of "starch paste." Different starches vary considerably in the temperature at which they gelatinize and in the physical properties of the paste produced. Thin starch pastes can be filtered through paper, but almost always leave some gelatinous residue upon the filter. Pastes containing only a few hundredths of one per cent of starch become clear on boiling and can be filtered without loss. Water-soluble starch can be prepared* by chemical treatment and is sometimes found in natural products, for example in immature grains.

Cellulose, and the ordinary pentosans of foods and fibers, are insoluble in water and not gelatinized by boiling.

In Alcohol and Ether.

Levulose is soluble in 5 parts of cold absolute alcohol and is somewhat soluble in mixtures of ether and strong alcohol. The other monosaccharides are sparingly soluble in cold alcohol, insoluble in ether and practically insoluble in the alcohol-ether mixture. Dextrose is much more readily soluble in hot than in cold alcohol; 100 parts of 90 per cent. alcohol dissolve about 2 parts dextrose at 18°, about 22 parts at boiling temperature.

The di-, tri-, and polysaccharides are insoluble in ether. Di- and trisaccharides are less soluble in alcohol than is dextrose. Lactose is practically insoluble in alcohol, even when the latter is diluted to 60 per cent.

Sucrose is much more readily soluble in diluted than in concentrated alcohol. According to Scheibler:

100	parts	90	per	cent.	alcohol	dissolve	0.9	parts	at	14°;	2.3	parts	at	40°.
"	"	80	"	"	"	"	6.6	"	"	"	13.3	"	"	"
"	"	70	"	"	"	"	18.8	"	"	"	31.4	"	"	"
"	"	60	"	"	"	"	33.9	"	"	"	49.9	"	"	"
"	"	50	"	"	"	"	47.1	"	"	"	63.4	"	"	"

* Lintner: *Journ. prakt. Chem.* 1886, [2] 34, 381. Wroblewski: *Ztschr. physiol. Chem.*, 1898, 24, 173. Vaubel: *Best. org. Verbind.*, II., 500.

Sucrose dissolves in about 80 parts of boiling absolute alcohol.

All of the polysaccharides are insoluble in alcohol. Those which are soluble in water can be precipitated from their aqueous solutions by the addition of strong alcohol.

In Acids and Alkalies.

Among the carbohydrates which are inslouble in water, separations can sometimes be made by the use of acid or alkaline solutions.

Cellulose is soluble in concentrated sulphuric acid, but insoluble in any ordinary aqueous solution of acid or alkali. It dissolves in Schweitzer's reagent (aqueous ammonia saturated with cupric hydroxide) to a viscous solution from which it is precipitated by neutralization with acid.

Starch is insoluble in Schweitzer's reagent or in solutions of ammonia. Treated with dilute aqueous solutions of sodium or potassium hydroxide, starch swells, gelatinizes and becomes soluble. It can be completely precipitated from such a solution by neutralizing with acetic acid and adding strong alcohol. Starch is not affected by dilute solutions of alkalies in strong alcohol. By diluted solutions of strong acids starch is first dissolved, then hydrolized. Some weak organic acids dissolve starch with little if any hydrolysis. Boiling water containing 1 per cent. of salicylic acid dissolves starch to an opalescent solution which filters much more readily than a corresponding starch paste made with water alone.

The pentosans of foods and fibers — so-called woodgums consisting mainly of xylan — are insoluble in dilute ammonia or in Schweitzer's reagent, largely soluble in dilute aqueous solutions of sodium or potassium hydroxide and in cold dilute acids. From such solutions the pentosan is precipitated by alcohol. Boiling dilute mineral acids dissolve and hydrolize pentosans almost as readily of starch. Hence pentosans have frequently been reported as starch when the latter has been estimated by direct hydrolysis with acid and determination of the resulting glucose.

REACTIONS WITH PHENYLHYDRAZINE.

All of the monosaccharides, and maltose and lactose among the disaccharides, contain the free carbonyl radical and, therefore, on treatment with phenylhydrazine acetate in molecular proportions, they react to form hydrazones. All of these hydrazones, except

that of mannose, are freely soluble in water. The formation of an insoluble hydrazone is a distinctive test for mannose, and has been applied as a quantitative method by Bourquelot and Herissey.*

When the hydrazone of a sugar is heated with an excess of phenylhydrazine, the hydroxyl adjacent to the hydrazone group undergoes oxidation and condensation resulting in the formation of the dihydrazone, more commonly known as the osazone. The osazones are only sparingly soluble in water, and on crystallization show definite forms and melting points. The formation of the osazone is, therefore, an important means of identification for sugars having the carbonyl radical.

Preparation and Properties of the Osazones.

To form the osazone,† dissolve one part of the sugar, two of pure phenylhydrazine hydrochloride and three of crystallized sodium acetate in 20 parts of water in a test-tube. Cork loosely to avoid evaporation and place the tube in boiling water.

If the substance tested is pure and the above proportions are maintained, the time required for the appearance of an osazone precipitate is fairly constant. These differences in the rate of osazone formation have been especially studied by Mulliken and play a prominent part in his system of identification of pure sugars. All of the monosaccharides, and no other carbohydrates, give precipitates within 20 minutes. Maltose and lactose form osazones which are much more soluble in hot water than those of the monosaccharides, and under the conditions given, separate from the solution only on cooling. Sucrose when subjected to this test is gradually hydrolyzed so that eventually it yields the osazone of dextrose and levulose. Under the conditions given, however, this requires about 30 minutes heating in the water bath.

In general, therefore, a precipitate appearing at the temperature of the water bath within 20 minutes indicates the presence of a monosaccharide; a slight precipitate of osazone appearing only on cooling might be due to a very small amount of monosaccharide, but any considerable quantity of osazone which precipitates

* *Journ. Pharm. Chim.*, 1899, [6], 10, 206. See also Pellet: *Bull. Assoc. Chim. Sucr. Distill.*, 1900–01, 18, 758; Abs. *Ztschr. Unters. Nahr. Genussm.*, 1902, 5, 74.

† Fischer: *Ber. deut. chem. Ges.*, 1884, 17, 579; 1887, 20, 821; 1888, 21, 1805, 2631; 1889, 22, 87; 1890, 23, 2117.

Mulliken: Identification of Pure Organic Compounds, Vol. I., p. 32.

only on cooling is indicative of lactose, maltose or isomaltose.

The maximum yield of osazone is usually obtained by warming the solution in the water-bath for one to two hours and then allowing it to cool. The osazone thus obtained is ordinarily a yellow iridescent precipitate, more or less distinctly crystalline according to the purity and concentration of the solution. To purify it, filter on a small paper, wash with a little cold water, dissolve in the smallest possible amount of boiling 50 per cent. alcohol and filter hot. The osazone which separates from the alcohol solution may, if desired, be further recrystallized from alcohol or from pyridine.

Dextose, levulose and mannose yield the same osazone, *glucosazone*, which crystallizes in needles melting at 204°-205° when heated at such a rate that the melting-point is reached in three to four minutes.* *Galactosazone* crystallizes in needles which melt at 193°; *maltosazone*, in independent needles or tables melting at 206°; *lactosazone*, in masses of microscopic prisms melting at 200°. *Xylosazone* and *arabinosazone* melt at about 160°.

A conclusive method of ascertaining whether an osazone is that of a pentose, a hexose or a disaccharide is to determine the percentage of nitrogen. In the case of a mixture the hexosazone can be freed from osazones of the other two groups by washing with hot water. Maltosazone is soluble in about 75 parts, xylosazone in about 50 parts, and lactosazone in 80 to 90 parts of boiling water, while the pure hexosazones are nearly insoluble.

The yield of osazone has been studied especially by Macquenne,† Laves,‡ Fischer,§ Lintner and Kröber,‖ Raimann,¶ and Davis and Ling.** In each of these cases the osazone was formed by heating for one or two hours, in a more dilute solution than that above given, with a considerable excess of a slightly acid solution of phenylhydrazine acetate. The precipitate of osazone can then be filtered, washed with water and weighed. According to Laves

* Any of the osazones on being heated very slowly may begin to melt considerably below the temperatures given.

† *Compt. rend.*, 1891, 112, 799; *Ztschr. anal. Chem.*, 1894, 33, 226.

‡ *Archiv. der Pharm.*, 1893, 231, 366; Vaubel's Bestimmung organischer Verbindungen, II., 307, 311, 312.

§ *Ber. deut. chem. Ges.*, 1895, 28, 1437.

‖ *Ztschr. f. d. ges. Brauwesen*, 1895, 18, 153; *Ztschr. anal. Chem.*, 1896, 35, 95; *Analyst*, 1897, 20, 167.

¶ *Ztschr. anal. Chem.*, 1901, 40, 390.

** *Journ. Chem. Soc.*, 1904, 85, 24.

the following corrections should be applied for the amount of glucosazone left in solution or dissolved by washing:

100 parts	boiling water	dissolve	0.01 part osazone.
100 "	water at 20°	"	0.0042 " "
100 "	2 per cent. acetic acid at 20°	dissolve	0.007 " "
100 "	3 " " " " " 20°	"	0.0145 " "
100 "	4 " " " " " 20°	"	0.022 " "
100 "	5 " " " " " 20°	"	0.031 " "
100 "	10 " "	alcohol slightly acidulated dissolve at 20°	0.0075 " "

Corresponding corrections have not been worked out for other osazones, as the attempts to apply the osazone method quantitatively have been mainly with the object of determining dextrose or dextrose and levulose. In comparative tests carried out in exactly the same manner, the weight of osazone obtained is proportional to the amount of sugar originally present, but slight differences of manipulation affect the yield to such an extent that the osazone precipitation cannot yet be regarded as a satisfactory quantitative method.

For the detection of dextrose, or invert sugar, in the absence of other monosaccharides, the osazone test may be applied as follows:* Dissolve 0.2 gram of sample (or, if only partially soluble, stir so much as contains 0.2 gram of soluble solids) in 4 c.c. of water, filter if necessary, add 0.40 gram phenylhydrazine hydrochloride and 0.60 gram crystallized sodium acetate; shake until dissolved, filter if not clear; place the solution, contained in a small test-tube corked loosely to prevent evaporation, in a beaker of boiling water and shake frequently without removing the tube from the water-bath.

The following results were obtained with solutions containing known amounts of pure sugars, the amounts of water and reagents and the manipulation being in each case as just described.

SOLUTIONS OF PURE DEXTROSE.

Dextrose present	0.10	0.05	0.02	0.01	0.005 gram.
Osazone appeared in	5	6½	10½	17–19	34 minutes.

SOLUTIONS CONTAINING 0.01 GRAM DEXTROSE, WITH VARYING AMOUNTS OF MALTOSE OR LACTOSE.

Maltose or Lactose present	0.01	0.05	0.10	0.20	gram
Osazone appeared in	22–25	30–32	37–46	†	minutes.

* Compare Mulliken, *loc. cit.*

† No precipitate of osazone appeared in the hot solution although the heating was continued for two hours.

These experiments, made by R. H. Williams in the course of an investigation which is still in progress in this laboratory, illustrate the delicacy of the test when only dextrose is present, and the influence of maltose and lactose in retarding the precipitation of dextrose as osazone. Sucrose up to ten times the weight of dextrose present had no appreciable influence. In larger proportion it may hasten very slightly the appearance of the osazone. As already explained sucrose tested alone undergoes gradual hydrolysis and thus finally gives a precipitate of glucosazone.

The delicacy of the test in the presence of dextrin (which is known to retard the formation of the osazone), and of substances other than carbohydrates, has not yet been studied in detail, except in the case of certain constituents of urine.* Hence in applying the osazone test to an unknown solution, it is well to make at the same time two check experiments, one with a mixture of carbohydrates corresponding to that which the unknown solution is believed to contain, the other with a portion of the unknown solution to which has been added a very small amount of dextrose.

REDUCTION OF ALKALINE COPPER SOLUTIONS.

The aldehyde and ketone sugars are easily oxidized and hence have the power of reducing certain metallic salts, especially salts of copper, silver and mercury in alkaline solution. The reagent most commonly used in detecting or determining sugars by their "reducing power," is prepared by treating cupric sulphate with an excess of an alkaline tartrate solution. When such an alkaline copper solution is boiled with any one of the aldehyde or ketone sugars (*i. e.*, with any carbohydrate capable of reacting with phenylhydrazine), the copper is reduced by the action of the sugar from the cupric to the cuprous state. In the case of a tartrate solution containing only fixed alkali, the reduced copper is precipitated as cuprous oxide. The changes which take place in the sugar are quite complex and only in the case of dextrose have the products been studied to any extent.

On boiling with the alkaline copper solution, dextrose is attacked in two ways:† (1) *Oxidation* to tartronic, gluconic, oxalic, acetic,

* The influence of other substances likely to be present, upon the osazone test for dextrose in urine has been studied by — Hirschl; *Ztschr. physiol. Chem.*, 1890, **14**, 377: Jaffé; *Ibid.*, **22**, 532: Neuberg; *Ibid.*, 1900, **29**, 274: Neuman-Wender; *Pharmac. Post.*, **26**, 573, 614 (Vaubel; *l. c.* II., 309).

† For fuller discussions of this subject see the works of Lippmann, Vaubel and Wiley cited below.

formic and carbonic acids, and probably other products which have not yet been recognized. (2) *Decomposition by alkali* into substances no more highly oxidized than the original sugar. Lactic acid is the most conspicuous of these, but other more complex products, including aromatic compounds and gummy substances of unknown constitution, are formed by rearrangement under the influence of the alkali. In practice less than half as much copper is reduced as would correspond to a complete oxidation of dextrose to tartronic acid, although the latter compound is probably the chief oxidation product formed. It is evident, therefore, that the decomposing action of the alkali, unless carefully controlled, will influence greatly the amount of copper reduced.

Fehling,* who first systematically studied the determination of reducing sugars by their action upon alkaline copper solutions, used a reagent containing 34.64 grams of crystallized copper sulphate, 138.6 grams of potassium tartrate and 47 to 55 grams of sodium hydroxide, the whole dissolved in water and diluted to one liter. Ten c.c. of this reagent were diluted with 40 c.c. of water and heated to boiling. A solution containing not more than 1 per cent. of dextrose or invert-sugar, was then added, until after two minutes boiling the solution contained no unreduced copper. Fehling held that under these conditions each molecule of dextrose or levulose reduced five atoms of copper from the cupric to the cuprous state. According to this proportion 10 c.c. of the Fehling reagent require for complete reduction exactly 0.05 grams of dextrose, levulose or invert sugar.

It has been found, however, that the ratio between dextrose and copper is constant only when the alkalinity and dilution of the solution are kept nearly uniform. According to Soxhlet,† one molecule of dextrose in 1 per cent. solution reduces 5.26 atoms of copper from undiluted Fehling solution or 5.055 atoms from the same solution diluted with four times its volume of water. Soxhlet recommended the use of 1 per cent. solutions of reducing sugars with undiluted Fehling solution under which conditions 10 c.c. of the latter are reduced by 0.0475 gram of dextrose. The use of undiluted Fehling solution has, however, the disadvantage that sucrose, if present, may be partially hydrolyzed by the boiling alkali thus causing high results, whereas the diluted Fehling solu-

* *Ann. Chem.*, 1849, 72, 106.

† *Jour. prakt. Chem.*, 1880 [2], 21, 227.

tion seems to be entirely without effect upon sucrose. Moreover, it is evident from the figures given by Soxhlet that at a slightly greater dilution, as when a solution containing 0.25 to 0.5 per cent. of dextrose is used, the ratio of Fehling is practically correct. Soxhlet also showed that the reducing power is constant only when the whole amount of sugar required for the reduction of the copper is added at once.

Many other modifications of Fehling's method have been proposed and a committee of the International Commission for Unifying Methods of Sugar Analysis is now (1905) investigating this subject with a view to the development of more satisfactory and uniform methods. Until some such international agreement is reached the volumetric determination of reducing sugars may conveniently be made by the following method, which is that of Fehling with only such modifications as have been generally recognized as essential to accuracy.

Fehling's Volumetric Method.

Reagents. — (1) Copper solution: Dissolve 34.64 grams of pure crystallized copper sulphate in water, and dilute to exactly 500 c.c.

(2) Alkaline tartrate solution: Dissolve 175 grams of pure sodium potassium tartrate and 50 grams of pure sodium hydroxide in water, and dilute to 500 c.c. This reagent does not keep well unless carefully protected from the air.

Determination. — Measure accurately into a small flask or casserole or a deep porcelain dish, 5 c.c. of each of the above solutions, making 10 c.c. of the "mixed Fehling reagent." Add 40 c.c. of water, mix and boil. To the boiling liquid, add from a burette a solution which is judged to contain about 1 per cent. of the sugar to be determined, until after two minutes boiling the blue color is entirely discharged showing that all of the copper has been reduced. This test indicates approximately the amount of reducing sugar in the sample. Now adjust the strength of the sugar solution, if necessary, so that between 10 and 20 c.c. will be required to reduce 10 c.c. of the mixed Fehling reagent. Repeat the test, adding the calculated amount of sugar solution at once to the boiling copper solution; regulate the heating so that the mixture will begin to boil about one minute after the addition of the sugar; note the exact time that actual boiling commences and continue to boil for just two minutes, then remove the flame and at once test the liquid for un-

reduced copper. This may be done in several ways. The method commonly recommended is to filter a portion of the liquid, acidulate with acetic acid and test for copper with potassium ferrocyanide. A more convenient method which appears to be equally reliable has recently been suggested by Harrison * and consists in adding a drop or two of the liquid (which need not be filtered from cuprous oxide) to a considerable excess of cold acidulated starch-iodide solution prepared as described below. Any unreduced copper causes a liberation of iodine with the production of a color varying from purplish red to deep blue according to the amount of copper in the solution. Until considerable experience has been acquired, it is well to make both tests, observing all the precautions noted below.

Repeat the test using more or less of the sugar solution depending upon the presence or absence of an excess of copper in the preceding experiment until two amounts of sugar solution are found which differ by only 0.1 or 0.2 c.c., one giving complete reduction and the other leaving a small amount of copper in the solution. The mean of the two readings is taken as the volume of solution required for complete reduction of the copper reagent.

Notes and Precautions. — All of the reagents used must be the purest obtainable and the two constituents of the "mixed Fehling reagent" must be kept separate instead of being made up in one solution as was formerly done. If the solutions are not fresh, make a blank test in a casserole, boiling as above without the addition of any sugar, allow to stand for a few minutes, then decant off the liquid and notice whether any cuprous oxide has been precipitated. Finally wipe out the casserole with a small piece of filter paper and examine the latter, which may show traces of cuprous oxide not visible in the presence of the blue solution. If the liquid shows any change of color in this blank test, or if the slightest trace of cuprous oxide is found, the alkaline tartrate solution must be rejected and another blank test made with a freshly prepared solution.

If the sample analyzed is rich in reducing sugar all of the quantities given above should be doubled in order to reduce the influence of unavoidable errors.

In testing for copper by the ferrocyanide method, great care must be taken to filter out all of the cuprous oxide quickly. This is best done by withdrawing the portion to be tested through the

* *Pharm. Journ.*, 1903, 170; Sutton's Volumetric Analysis (9th Ed.), p. 312.

filtering tube described by Wiley * or by pouring it carefully upon a double or triple paper filter. A single filtration through one ordinary paper seldom removes all of the cuprous oxide. On the other hand if a slight trace of unreduced copper is present this may sometimes be lost by repeatedly passing the solution through several thicknesses of paper. Traces of iron getting into the solution from reagents or apparatus may cause a slight coloration with ferrocyanide. Only a distinct red-brown precipitate or coloration should be taken as showing the presence of unreduced copper.

The starch-iodide solution for detecting unreduced copper without filtration is prepared as follows: Boil 0.02 gram starch with 15 to 20 c.c. of water, cool, add 4 to 5 grams potassium iodide and dilute to 50 c c. A fresh solution must be prepared each day. When the test is to be made pour about 1 c.c. of the starch-iodide into a test-tube, add two or three drops of acetic acid and then immediately a drop or two of the solution to be tested.

Calculation and Verification of Results. — In calculating the results it is commonly assumed that 10 c.c. of the mixed Fehling reagent require for reduction under the above conditions:

0.0500 gram of anhydrous dextose, levulose or invert sugar.
0.0678 " " dry crystallized lactose ($C_{12}H_{22}O_{11} \cdot H_2O$).
0.0807 " " anhydrous maltose.

That these factors are not absolute, but are dependent upon exact uniformity of conditions has already been explained. To secure the greatest accuracy, therefore, the result obtained should be verified by a check experiment, carried out under the exact conditions of the analysis, with a known solution of pure sugar of the kind actually determined.

According to Soxhlet, levulose and galactose have distinctly less reducing power than dextrose. It is quite commonly assumed, however, that these three monosaccharides have the same reducing power, but that invert sugar often fails to show its full effect because of the decomposing action of the acid used for inversion. Xylose and arabinose reduce Fehling solution somewhat more strongly than does dextrose.

Substitution of Other Methods.

Aside from modifications in detail, several methods intended to replace that of Fehling have been proposed. In some of these the

* Agricultural Analysis, Vol. III., p. 130.

caustic alkali of Fehling's solution is replaced by a weaker base, such as alkaline carbonate or bicarbonate (Soldani, Sidersky, Ost) or ammonia (Allein and Gaud); in others, ammonia (Pavy) or cyanide (Gerrard) is added to the usual Fehling reagent in order to hold in solution the reduced copper, so that the point of complete reduction can be directly observed by the disappearance of the blue color. More important, however, are the methods in which, as described below, a fixed volume of the sugar solution is boiled with an excess of the alkaline copper solution and the reduced copper collected and determined.

Defren's Gravimetric Method.*

This method is based on that of O'Sullivan † and provides a uniform procedure for the determination of dextrose, maltose or lactose.

Reagents. — (1) Dissolve 34.64 grams of copper sulphate in water, add 0.5 c.c. strong sulphuric acid and dilute to 500 c.c.

(2) Dissolve 178 grams of sodium potassium tartrate and 50 grams of sodium hydroxide in water and dilute to 500 c.c.

Determination. — Mix 15 c.c. of each of the above reagents in an Erlenmeyer flask having a capacity of 250 to 300 c.c., dilute with 50 c.c. of freshly boiled distilled water and place the flask in a boiling water-bath for five minutes; then add 25 c.c., accurately measured from a burette or pipette, of a solution containing approximately 0.5 per cent. of the sugar to be determined and allow the mixture to stand in the boiling water-bath for fifteen minutes. Remove the flask from the bath and filter as quickly as possible (using moderate suction) through asbestos prepared as described below; wash the cuprous oxide with boiling distilled water until the filtrate is no longer alkaline. The cuprous oxide can now be (1) washed with alcohol and then with ether, dried in a boiling water oven for 20 minutes and weighed; (2) ignited and weighed as cupric oxide, as recommended by Defren; or (3) dissolved in nitric acid and the copper determined by electrolysis or by any other reliable method in which case it will not be necessary to use asbestos especially prepared by boiling with acid and alkali. From the weight of copper or cuprous oxide determined, calculate the equivalent amount of cupric oxide and find the corresponding weight of reducing sugar from Defren's table.

* *Journ. Amer. Chem. Soc.*, 1896, 18, 749.

† *Journ. Chem. Soc.*, 1876, 30, 130.

Precautions. — If the copper reduced is to be weighed as cuprous or cupric oxide on the asbestos filter, the latter must be especially prepared in order that it shall lose no weight when treated with the hot alkaline Fehling solution. Asbestos of good quality is boiled with nitric acid (1.05 to 1.10 sp. gr.) washed with water then boiled with 25 per cent. sodium hydroxide, washed, and the treatment with acid and alkali repeated. The prepared asbestos is used to make a tight felt about one centimeter thick in a Gooch crucible. When the crucible has been prepared for use and weighed it should be tested by running through it a "blank" of hot alkaline Fehling solution and washing with water as in a regular determination. The loss of weight should not exceed one half milligram. After each determination the precipitate is dissolved in nitric acid and the crucible washed, ignited and reweighed. If a loss of over one milligram is found, the determination should be rejected and the filter treated alternately with acid and alkali until it ceases to lose in weight.

Notes on Defren's Table. — Defren determined the amount of copper reduced by fifteen to twenty known solutions each of dextrose, maltose and lactose with the following results:

$$\text{Dextrose} = (0.4400 + 0.000037\ W)W.$$
$$\text{Maltose} = (0.7215 + 0.000061\ W)W.$$
$$\text{Lactose} = (0.6270 + 0.000053\ W)W.$$

In which W is the weight of cupric oxide obtained, the values of W varying from 30 to 320 milligrams.

From these formulæ it is apparent that the reducing power of each of the sugars increases slightly with the concentration, as was found to be the case in Soxhlet's volumetric method.

This table is condensed from that given in Defren's paper (*l. c.*) in which the weights of sugars corresponding to each milligram of cupric oxide are stated. In using either table the weight of copper or cupric oxide should be taken to one-tenth milligram and the corresponding weight of reducing sugar found by the method of proportional parts. The table on the following page is based on these equations:

Defren's Table for Dextrose, Maltose and Lactose.

Cupric Oxide mgms.	Dextrose mgms.	Maltose mgms.	Lactose mgms.	Cupric Oxide mgms.	Dextrose mgms.	Maltose mgms.	Lactose mgms.
30	13.2	21.7	18.8	180	80.4	131.8	114.6
40	17.6	29.0	25.2	190	84.9	139.1	121.0
50	22.1	36.2	31.5	200	89.5	146.6	127.5
60	26.5	43.5	37.8	210	94.0	154.1	134.1
70	30.9	50.8	44.1	220	98.6	161.5	140.6
80	35.4	58.1	50.5	230	103.1	169.1	147.0
90	39.9	65.5	56.8	240	107.7	176.6	153.5
100	44.4	72.8	63.2	250	112.3	184.1	160.0
110	48.9	80.1	69.5	260	116.9	191.6	166.5
120	53.3	87.4	75.9	270	121.4	199.2	173.0
130	57.8	94.8	82.4	280	126.1	206.8	179.6
140	62.2	102.1	88.7	290	130.7	214 3	186.2
150	66.8	109.5	95.2	300	135.3	221.9	192.8
160	71.3	116.9	101.7	310	139.9	229.6	199.3
170	75.8	124.4	108.2	320	144.5	237.2	205.9

KJELDAHL'S GRAVIMETRIC METHOD. *

As the result of study of many of the conditions affecting the gravimetric determination of reducing sugars, Kjeldahl recommended the following method:

Reagents.—(1) Copper Solution: 34.65 grams of pure crystallized copper sulphate in 500 c.c. (2) Alkaline Solution: 65 grams of sodium hydroxide, determined by titration, in 500 c.c. (3) Pure sodium potassium tartrate pulverized and kept in the dry state.

Determination. — In an Erlenmeyer flask holding about 150 c.c., mix 5.2 grams of sodium potassium tartrate and 15 c.c. each of the alkaline and copper solutions† add a known volume of the sugar solution, which must not contain over 0.140 gram of dextrose or an equivalent amount of other reducing sugar, and fill with water to 100 c.c.; close the flask with a two-holed stopper and pass a current of hydrogen or illuminating gas until all air is expelled from the flask; stand the flask in a boiling water bath for exactly 02 minutes; filter, and determine the reduced copper as described under Defren's method. Find the corresponding weight of reducing sugar from the table on the opposite page.

* *Midelelser fra Carlsberg Lab.*, 1895, 5, 1; Abs. *Analyst*, 1895, 20, 227; *Ztschr. anal. Chem.* 1896, 35, 344; Bujard and Baier's Hilfsbuch für Nahrungsmittelchemiker, Berlin, 1900.

† This gives practically 30 c.c. of the "mixed Fehling reagent" containing the same quantity of copper as is used in Defren's method. Kjeldahl's method also includes directions and tables for the use of 15 c.c. or 50 c.c. of the mixed copper reagent if necessary. The proportions here given are adapted to such solutions as would usually be obtained in the estimation of reducing sugars.

Kjeldahl's Table for Reducing Sugars.

Copper mgms.	Dextrose mgms.	Levulose mgms.	Invert-Sugar mgms.	Galactose mgms.	Lactose $C_{12}H_{22}O_{11}+H_2O$ mgms.	Maltose $C_{12}H_{22}O_{11}$ mgms.
40	17.8	19.8	19.1	19.8	26.7	30.9
50	22.4	24.9	23.9	25.0	33.6	38.8
60	27.0	30.1	28.8	30.1	40.6	46.8
70	31.8	35.2	33.8	35.4	47.6	54.8
80	36.6	40.5	38.8	40.7	54.6	63.0
90	41.4	45.9	43.9	46.0	61.8	71.2
100	46.4	51.3	49.1	51.5	69.0	79.4
110	51.4	56.8	54.4	57.0	76.4	87.7
120	56.6	62.4	59.8	62.6	83.8	96.1
130	61.8	68.0	65.2	68.3	91.3	104.7
140	67.1	73.7	70.7	74.0	98.9	113.3
150	72.5	79.6	76.3	79.9	106.5	121.9
160	78.0	85.5	82.0	85.8	114.3	130.7
170	83.7	91.5	87.9	91.9	122.2	139.6
180	89.4	97.6	93.8	98.0	130.3	148.6
190	95.3	103.9	99.9	104.3	138.4	157.6
200	101.4	110.2	106.1	110.6	146.7	166.8
210	107.5	116.7	112.4	117.1	155.0	176.1
220	113.9	123.2	118.8	123.8	163.5	185.5
230	120.4	130.0	125.5	130.5	172.2	195.1
240	127.1	136.8	132.2	137.5	181.0	204.7
250	134.1	143.8	139.2	144.5	189.9	214.4
260	141.2	150.9	146.3	151.8	199.0	224.3

Barfoed's Cupric Acetate Method.*

For the detection of dextrose Barfoed used a slightly acid solution of cupric acetate in place of the Fehling solution. Lieben attempted to determine dextrose quantitatively in the presence of maltose by means of such solutions. This test, like the formation of the osazone, is not of much quantitative value unless for comparisons under identical conditions, but is often useful as a qualitative method for distinguishing between dextrose (or other monosaccharide) and those disaccharides which also reduce Fehling's solution.

Reagent. — Dissolve 45 grams of neutral crystallized cupric acetate in 900 c.c. of water, filter if necessary; add 1.2 c.c. of 50 per cent. acetic acid and dilute to a liter. A portion of this reagent heated in a water-bath must show no change.

Test. — To 5 c.c. of this reagent in a test-tube add 5 c.c. of the solution to be tested and place in a boiling water-bath for 3½ minutes; examine for cuprous oxide, viewing the tube against a black background in a good light. If no evidence of reduction is found,

* Barfoed: *Ztschr. anal. Chem.*, 1873, 12, 27. Müller and Hagen: *Arch. ges. Physiol.* (*Pflüger*), 22, 325. Lieben: *Ztschr. Vereins Rübenzucker-Industrie*, 1884, 34, 857; Wiley, Agricultural Analysis, Vol. III., p. 291.

allow the tube to stand at room temperature for 10 minutes and examine again.

Notes. — Under the conditions given maltose and lactose do not reduce the reagent. Longer heating or the use of a more acid solution causes a reduction due to the hydrolysis of the disaccharide. In order to prevent this, the solution may be heated to 40° only. At this temperature, however, dextrose reduces very slowly so that the heating must be continued for several hours.

Recent experiments have shown that the test as described is capable of distinguishing between dextrose and maltose in aqueous solutions containing less than 0.02 per cent. of the former and at least 0.2 per cent. of the latter, provided the results are controlled by check experiments made under identical conditions with solutions containing known amounts of dextrose and maltose. Dextrin does not interfere.

If the solution tested contains proteids these are precipitated by the copper, rendering the test slightly less delicate.

In applying the reaction to an unknown solution, comparative tests should be made as directed in the case of the phenylhydrazine test.

REACTIONS WITH ACIDS.

All carbohydrates on treatment with moderately strong hydrochloric or sulphuric acid yield furfurol, which is probably the cause of the color reaction with α-naphthol described below. Hexa-carbohydrates form only small amounts of furfurol and relatively large amounts of levulinic acid. Penta-carbohydrates yield large amounts of furfurol and no levulinic acid. In all cases, however, there is more or less formation of "humus" and other by-products

MOLISCH'S α-NAPHTHOL REACTION.*

Mix 2 to 3 c.c. of the very dilute solution to be tested with 2 or 3 drops of a 15 per cent. solution of α-naphthal in alcohol or chloroform, incline the tube and pour in carefully 2 to 3 c.c. of pure concentrated sulphuric acid. In the presence of carbohydrate, a violet zone appears quickly and spreads by diffusion. If the solution tested contains more than a few milligrams of carbohydrate, it

* Molisch: *Monatsh. Chem.*, 1886, 7, 198.
Udranszky: *Ztschr. physiol. Chem.*, 1888, 12, 355, 377.
Tollens: Handbuch der Kohlenhydrate, II., 101.
Mulliken: Identification of Pure Organic Compounds, I., 26.

quickly blackens and on dilution with water gives a dull violet precipitate.

A similar test with thymol gives a crimson or carmine-red solution which soon becomes turbid.

Furfurol Test for Pentoses and Pentosans.

Place the substance to be tested in an Erlenmeyer flask, add hydrochloric acid (1.06 sp. gr.) and boil. Lay over the mouth of the flask a small filter paper moistened with a solution of anilin acetate.* If the vapor escaping from the flask contains more than traces of furfurol a bright red coloration appears. A test with sucrose or pure starch will show the amount of color to be expected from hexa-carbohydrates.

If the reaction obtained from the unknown substance is much stronger than from sucrose or starch, the presence of pentoses or pentosans is indicated. A few other substances such as glycüronic acid and oxycellulose have been found to yield considerable amounts of furfurol, but these rarely occur in sufficient quantities to require consideration.

Determination of Pentoses and Pentosans.

Under carefully regulated conditions the yield of furfurol from either xylose or arabinose, or from the corresponding anhydride, is nearly constant. If the furfurol is distilled and collected, its amount can be estimated by adding anilin acetate and comparing the red color with that shown by furfurol solutions of known strength.† This method is delicate, but gives only approximate results. Unless the quantity is very small, it should be determined gravimetrically.

Furfurol forms sparingly soluble condensation products with a number of bases and phenols. Phenylhydrazine and phloroglucin have been principally used as precipitants.‡ The Association of Official Agricultural Chemists has adopted provisionally the phloroglucin method in the following form:§

Three grams of the material are placed in a flask, together with

* Prepared by mixing equal volumes of anilin and 50 per cent. acetic acid.

† This colorimetric method is also used for the estimation of furfurol in distilled liquors.

‡ Barbituric acid has recently been recommended as preferable to phenylhydrazine and phloroglucin as a precipitant for furfurol. Unger: Dissertation, Munich, 1904. Jäger and Unger: Ber. deut. chem. Ges., 1902, 35, 4440.

§ Bull. 46, Bur. Chem., U. S. Dept. Agriculture. For a review and discussion of the methods of determining the pentosans and the practical applications of the results see Tollens, Kröber and Rimbach: *Ztschr. angew. Chem.*, 1902, 15, 477, 508. Also Fraps: *Amer. Chem. Journ.*, 1901, 25, 501.

100 c.c. of 12 per cent. hydrochloric acid (sp. gr. 1.06) and several pieces of recently heated pumice stone. The flask, placed upon wire gauze, is connected with a condenser and heat applied, rather gently at first, using a gauze top to distribute the flame, and so regulated as to distill over 30 c.c. in about ten minutes. The 30 c.c. driven over are replaced by a like quantity of the dilute acid, and the process continued so long as the distillate gives a pronounced reaction with anilin acetate on filter paper. To the completed distillate is gradually added a quantity of phloroglucin (free from diresorcin) dissolved in 12 per cent. hydrochloric acid, and the resulting mixture thoroughly stirred. The amount of phloroglucin used should be about double that of the furfurol expected. The solution turns first yellow, then green; and very soon an amorphous greenish precipitate appears, which grows rapidly darker, till it finally becomes almost black. The solution is made up to 500 c.c. with 12 per cent. hydrochloric acid, and allowed to stand over night.

The amorphous black precipitate is filtered into a tared gooch through an asbestos felt, washed with 100 c.c. of water, dried to constant weight by heating from three to four hours at 100°, cooled and weighed, the increase in weight being reckoned as phloroglucid. To calculate the furfurol from the phloroglucid, the following formulæ are used:

Phloroglucid (less than and up to 0.2 gram) ÷ 1.82 = furfurol.
Phloroglucid (from 0.2 to 0.3 gram) ÷ 1.895 = furfurol.
Phloroglucid (from 0.3 to 0.4 gram) ÷ 1.92 = furfurol.
Phloroglucid (above 0.4 gram) ÷ 1.93 = furfurol.

To the weight of furforal thus found, 0.0104 gram is added as a correction for solubility and the corrected weight is multiplied by 1.91 for xylose, 2.35 for arabinose or 2.13 for "pentose."

Qualitative test of the purity of the phloroglucin.— Dissolve a small quantity of the phloroglucin in a few drops of acetic anhydrid, heat almost to boiling and add a few drops of concentrated sulphuric acid. A violet color indicates the presence of diresorcin. A phloroglucin which gives more than a faint coloration must be rejected.

Levulinic Acid Reaction of Hexa-carbohydrates.

According to Wehmer and Tollens,* all hexa-carbohydrates yield levulinic acid in sufficient quantity for identification when treated as follows:

* *Ann. Chem.*, 1887, 243, 314.

Heat 5 to 20 grams of the substance with 100 c.c. of hydrochloric acid (1.10 sp. gr.) for 18 hours on a boiling water-bath; filter the solution, shake with ether to extract the levulinic acid, and convert the latter into the zinc or silver salt for identification. As this method is purely qualitative and is not often used in ordinary analytical work, reference must be made to the original paper for details of manipulation.

Oxidation by Nitric Acid.

By heating with moderately strong nitric acid, xylose and arabinose are oxidized, each yielding a trioxyglutaric acid, $COOH(CHOH)_3COOH$, while aldoses of the hexose group yield the corresponding acids, $COOH(CHOH)_4COOH$, saccharic, mannosaccharic and mucic acids being obtained respectively from dextrose, mannose and galactose.

All of these oxidation products are freely soluble except mucic acid, which is practically insoluble in water or dilute nitric acid. Since mucic acid is produced in fairly constant proportion, its insolubility affords a means for the approximate determination of galactose or any substance which yields galactose on hydrolysis.

*Mucic Acid Method for Galactose, Lactose, Raffinose and Galactans.**

Weigh 1 to 3 grams of substance according to the amount of mucic acid expected; remove fat if necessary by washing with ether; transfer to a beaker about 5.5 cm. in diameter and 7 cm. deep; add 60 c.c. of nitric acid of 1.15 sp. gr. and evaporate the solution to exactly one hird its volume on a water-bath at a temperature of 94° to 96°. After standing 24 hours, add 10 c.c. of water to the precipitate and allow it to stand another 24 hours. The mucic acid has now crystallized, and unless contaminated with insoluble residue from the sample, it can be transferred to a weighed filter, washed with 30 c.c. of water, then with alcohol and ether, dried at 100° and weighed.

In case other insoluble substances are present, return the filter and mucic acid, after washing with water, to the beaker; warm 15 minutes with a mixture of 1 part strong ammonia, 1 part ammonium carbonate and 19 parts of water; filter and wash; evaporate filtrate to dryness over a water-bath; add 5 c.c. nitric acid of 1.15 sp.

* Tollens and Rischbiet: *Ber. deut. chem. Ges.*, 1885, 18, 2616. Creydt: *Ibid.*, 1886, 19, 3115. Bull. 46, Bur. Chem., U. S. Dept. Agriculture.

gr.; stir thoroughly and allow to stand for 30 minutes. Collect the mucic acid on a weighed filter, wash with 10 to 15 c.c. of water, then with 60 c.c. of alcohol and a number of times with ether; dry at 100° and weigh.

When these directions are strictly followed galactose yields about three fourths its weight of mucic acid. The weight of mucic acid obtained from lactose, raffinose or galactan is calculated as three fourths the weight of galactose which could be obtained by hydrolysis. The yield of mucic acid is, however, considerably influenced by the details of manipulation. In carrying out the method a comparative determination with pure milk sugar should always be made, as substances may be present which prevent the crystallization of the mucic acid.*

Hydrolysis by Dilute Acids.

Monosaccharides, as the name implies, cannot be hydrolyzed to simpler sugars. As a rule, they are unaffected by dilute acids except on prolonged heating, when they are gradually attacked, yielding in part decomposition products like those produced by stronger acids, and undergoing a partial "reversion" with the formation of di- or polysaccharides. Dextrose, for example, when heated too long with dilute hydrochloric or sulphuric acid, is changed partially to "isomaltose" and to dextrin-like anhydrides, such as "gallisin," the unfermentable constituent of crude commercial glucose. Levulose decomposes much more readily than dextrose on heating with dilute acids.

Disaccharides differ considerably in the readiness with which they are hydrolyzed by acids. Sucrose is very easily hydrolyzed, a 20 per cent. solution being completely changed to invert-sugar by mixing with one-tenth its volume of concentrated hydrochloric acid (making about 3 per cent. of actual acid in the mixture) and warming to 68° at such a rate as to require 15 minutes heating.†

Maltose is less easily hydrolized than sucrose, a 2 per cent. solution in 2 to 3 per cent. hydrochloric acid requiring 30 to 40 minutes' boiling, or 2 to 3 hours' heating on a water bath, for com-

* Herzfeld: *Ztschr. Vereins Robenzucker Ind.*, 1890, 40, 265; Abs. *Chem. Ztg.*, 1890, 14 *Rep.*, 108. Stone and Baird: *Jour. Amer. Chem. Soc.*, 1897, 19, 119.

† Clerget's method, described by Wiley: Agricultural Analysis, Vol. III., pp. 105–107. According to Borntträger and to Samelson (*Ztschr. angew. Chem.*, 1892, 334; 1893, 690; 1894, 267, 351), the sucrose in such a mixture is completely hydrolyzed by standing overnight at room temperature.

plete hydrolysis to dextose.* Lactose is also less readily hydrolyzed than sucrose, the difference being especially marked in the case of weak acids. By boiling with citric acid, sucrose can be completely converted to invert sugar, while lactose remains unchanged. (See methods for sucrose and lactose given below.)

Raffinose is hydrolyzed by dilute mineral acids, slowly in the cold, much more rapidly on boiling, requiring in either case more vigorous treatment than does sucrose.

Dextrin, glycogen and starch are hydrolyzed to dextrose under the same conditions as maltose, but require somewhat longer heating. Pentosans and galactans (at least the more common forms) are hydrolyzed by acids almost as readily as starch. Normal cellulose is not hydrolyzed by boiling dilute acids. Hemicellulose is a term commonly applied to the carbohydrate matter in the cell walls of plants, more resistant to enzymes than starch, but dissolved and hydrolyzed on boiling with dilute mineral acids. The hemicellulose of the common food plants consists largely of pentosans.

ROTATION OF POLARIZED LIGHT.

Solutions of the natural carbohydrates have the property of rotating the plane of polarized light. This rotating power is also shown by most other natural substances containing one or more asymmetric carbon atoms in the molecule.

MEASURE OF ROTATING POWER — SPECIFIC ROTATION.

The first organic substances to be studied by means of polarized light were liquids, or solutions of known density. In order to reduce the observations to a common basis for comparison Biot introduced the following formula :

$$[a] = \frac{a}{l \times d}$$

in which $[a]$ = the "specific rotating power"
a = the observed angular degrees of rotation
l = the length in decimeters of the column of liquid traversed by the polarized light
d = the density of the liquid.

* It is sometimes stated that maltose cannot be made to yield more than about 98 per cent. of the theoretical amount of dextrose, the acid always beginning to attack the latter before the hydrolysis of the former is quite complete. See notes on the determination of starch.

On extending the calculation to solids in solution the above formula becomes

$$[\alpha] = \frac{100\ a}{l \times d \times p}$$

in which $p =$ the percentage of solid in the solution.

But since $d \times p$ equals the number of grams of solid in 100 c.c. of solution it is simpler to write the formula

$$[\alpha] = \frac{100\ a}{l \times c}$$

in which $c =$ concentration, *i. e.*, the number of grams of dissolved solid in 100 c.c. of the solution.

The value of the specific rotating power $[\alpha]$ is, therefore, the number of angular degrees through which a ray of polarized light would be rotated in traversing one decimeter of a solution of which each cubic centimeter contained one gram of the active substance.

The angular rotation is always directly proportional to the length of the column of liquid through which the light passes. It always depends upon the wave length of the light ray employed. By measuring the rotation for different rays the rotation-dispersion of the substance is determined. Sodium light corresponding to the Fraunhofer line *D* is commonly used in determining the rotating power. In many cases the rotating power is appreciably influenced by temperature. The latter should therefore be stated in giving the value of $[\alpha]$. Thus $[\alpha]_D^{20}$ indicates the rotating power as measured with *D* light at 20°. The concentration of the solution has usually an appreciable influence upon the value of $[\alpha]$ as is shown by the following statements of rotating power of the more important carbohydrates:

Dextrose (Tollens)*

$$[\alpha]_D^{17} = \dagger\ 52.50 + 0.018796p + 0.0005168p^2.$$

Levulo ngfleish and Grimbert) ‡

$$[\alpha]_D^{t} = -[101.38 - 0.56t + 0.108(c - 10)].$$

Galactose (Meissl)§

$$[\alpha]_D^{t} = 83.883 + 0.0785p - 0.209t.$$

* *Ber. deut. chem. Ges.*, 1876, 9, 487, 1531; 1884, 17, 2234.

† Unless otherwise stated the rotation is to the right (+); lævorotation is indciated by (—).

‡ *Compt. rend.*, 1888, 107, 390.

§ *Journ. prakt. Chem.*, 1880, [2], 22, 97.

Sucrose (Tollens) *

$$[\alpha]_D^{20} = 66.386 + 0.015035p - 0.0003986p^2.$$

Lactose (Schmöger)†

$$[\alpha]_D^{20} = 52.53 \text{ (constant for } c = 2.4 \text{ to } 40).$$

Maltose (Meissl)‡

$$[\alpha]_D^{t} = 140.375 - 0.01837p - 0.095t.$$

At ordinary concentrations and laboratory temperatures, the values for $[\alpha]_D$ are approximately :

Dextrose	53	Sucrose	66.5
Levulose	$-[102 - .56t]$	Lactose	52.5
Invert-sugar	$-[27.9 - .32t]$	Maltose	138.
Galactose	80.5	Raffinose	104.5
Mannose	13	Starch, Glycogen	190 to 210
Arabinose	104	Dextrins	160 to 210
Xylose	19		

PREPARATION OF SOLUTIONS FOR POLARIZATION.

Reducing sugars when first dissolved often show rotating powers varying greatly from those given. This property, known as multirotation, or birotation, occasionally causes errors in analytical work. The normal rotation is established by allowing the solution to stand for some hours, by boiling, or by the addition of about 0.1 per cent. of ammonia. Solutions containing ammonia darken on standing and should therefore be polarized as soon as prepared.

Sucrose does not show multirotation, and is not appreciably affected by ordinary changes of temperature, while the changes of rotating power due to variations in concentration are small and have been accurately determined.

Solutions for polarization must be clear and free from all impurities having an influence upon polarized light. Among the optically active substances most likely to be met in natural products are organic acids (especially tartaric), pectin bodies, gums, resins, coloring matters, glucosides, alkaloids and proteids. In most cases the interfering substances can be precipitated and the solution clarified by adding, first, basic lead acetate, and then a cream of aluminium hydroxide. It is sometimes advantageous to add a small amount of tannin before clarifying. Tannin combines with many of the substances mentioned, either precipitating them or forming

* *Ber. deut. Chem. Geo.*, 1877, 10, 1403.

† *Ibid.*, 1880, 13, 1922.

‡ *Journ. prakt. Chem.*, 1882, [2], 25, 114.

compounds more easily precipitated by the basic acetate. In case the solution, after being treated with clarifying agents, made up to definite volume and filtered, is too highly colored for examination in the polariscope, it may be poured slowly through a small amount of pure, dry animal charcoal on a paper filter. Since the charcoal absorbs a small amount of the sugar, the first portions of the filtrate must be rejected.

Determination of Angular Rotation.

For the direct determination of $[\alpha]_D$, sodium light must be used. The instrument most commonly employed is the Laurent polariscope. This has a circular scale graduated in angular degrees. The scale is divided into half-degrees and the vernier is graduated to read minutes of angular rotation. With this polariscope the rotation produced by the active substance is found by turning the analyzing prism, which is fixed in position with regard to the scale, but rotates on its axis. The zero point is found with the polariscope empty and is the point at which the crystal axis of the analyzing prism is at right angles to the plane of polarization. If now an active substance is placed between the polarizing and analyzing prisms, the latter must be rotated until it stands at right angles to the new plane, when the appearance of the field will be the same as that previously observed at the zero point. The position of the scale now shows directly the number of angular degrees through which the plane of polarization has been rotated by the active substance.

For the examination of sugar solutions, especially in technical analysis, the Schmidt and Haensch saccharimeter with Ventzke scale, is commonly used. This instrument, which is made in several forms, is different in principle from the Laurent polariscope. White light is used and the rotation, instead of being measured directly, is "compensated" by means of quartz wedges, the thickness of quartz required to neutralize the effect of the active substance giving a means of the rotation produced by the latter. With the trough of the saccharimeter empty, the scale should read zero when the quartz wedges are so placed that the light passes through equal thicknesses of positive (dextrorotatory) and negative (lævorotatory) quartz. If now a tube containing a solution of sucrose is introduced, the thickness of negative quartz is increased, or that of positive quartz diminished, until the rotation produced

by the sugar solution is compensated by the opposite rotation of the quartz. This method of measuring the rotation by means of quartz with white light illumination is applicable only to such active bodies as have practically the same rotation dispersion as quartz. This is true of aqueous sugar solutions, which can therefore be examined by either of the instruments mentioned. The readings are compared by assuming that each degree of the Ventzke sugar scale is equivalent to 0.3468 degrees of angular rotation.

For descriptions of apparatus and details of testing and manipulation, the standard works on sugar analysis should be consulted. A number of the more important of these are among the reference books listed below, but attention may be especially directed to the work of Landolt as containing the most exhaustive and authoritative discussion of polarized light and its analytical applications.

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CHAPTER VI.

Carbohydrates—Special Methods.

ANALYSIS OF RAW SUGAR.

Polariscopic Examination.

A special room of even temperature which can be darkened when desired should be provided for the polariscopic examination. For illumination of the white-light saccharimeter, a triple flame or an Argand burner with incandescent mantle is used. In taking readings the polariscope must be brought only near enough to the burner to secure a good illumination of the field, never within less than eight inches. As soon as the reading is taken the polariscope should be turned away or the flame lowered, in order to avoid any possible warming of the instrument.

Determination of the Zero Point. — The trough of the saccharimeter being empty, set the scale within a few degrees of zero and focus the eyepiece so that the field of vision is clear and the perpendicular line or band dividing it is perfectly distinct. Now rotate the milled head so as to move the zero point of the scale toward that of the vernier. When the neutral point (the true zero point for the instrument as it stands) is reached the appearance of the entire field is uniform. Approach the zero point first from one side then from the other, taking the reading each time as soon as the field appears uniform, until successive readings do not differ by more than 0.2° on the Ventzke sugar scale. The average of ten such readings is taken as the zero point in all subsequent work with the instrument unless it should be jarred or moved, in which case the zero point should be redetermined.

Test with Pure Sugar.—Weigh 26* grams of pure sucrose, dis-

* The value of the Ventzke scale was originally fixed by means of pure sucrose solutions of 1.100 sp. gr. at 17.5° and it was found that 100 c.c. of such a solution contains 26.048 grams of sucrose (weighed in air with brass weights). For many years, however, it has been the custom of instrument makers to calibrate the Ventzke scale by means of solutions containing 26.048 grams of sucrose in 100 Mohr's cubic centimeters. A solution of very nearly the same strength is obtained by dissolving 26 grams and completing the volume at 20° to 100 metric cubic centimeters (the volume occupied by 100 grams of water at 4° weighed in vacuo). The latter proportions have recently been adopted by the International Commission for Unifying Methods of Sugar Analysis.

solve in water in an accurately calibrated 100 c.c. flask, fill to the mark at 20° to 22° and mix throughly by shaking, holding the flask in such a way as not to warm the solution. The latter should have a density very nearly 1.10 and should rotate the plane of polarized light 34.68° to the right, giving a reading of 100.0° on the Ventzke scale.

Rinse the 200 mm. tube several times with the solution, then fill until the curved surface of the liquid projects above the open end of the tube; see that all air-bubbles have risen to the surface and then slide on the cover-glass horizontally in such a manner that the excess of liquid is carried over the side, leaving the cover-glass exactly closing the tube, with no air-bubbles beneath it and none of the liquid upon its upper surface. The cover-glass being in position, the tube is closed by screwing on the cap. The latter should be only tight enough to prevent leakage, as any considerable pressure on the glass plate may cause it to become optically active.

Place the tube in the trough of the saccharimeter or polariscope and take ten readings as in setting the zero point. The average reading (corrected for zero point) should not differ from 100.0° by more than 0.2° on the Ventzke scale, nor from 34°41′ on the Laurent polariscope, by more than 5′.

Polarization of the Raw Sugar.—Mix the sample, weigh out 26 grams and dissolve in 60 to 80 c.c. of water in a 100 c.c. flask. When the sugar is entirely dissolved, add from 1 to 5 c.c. (according to the nature of the sample; only very dark sugars should require more than 2 c.c.) of a solution of basic lead acetate of about 1.25 sp. gr.* A decided excess of basic acetate should never be used. After the lead acetate has been added and mixed, add twice its volume of "alumina cream." † This assists in the clarification, precipitates the excess of lead, and facilitates filtration. A moderate excess of alumina cream does no harm. With high grade

* This may be prepared by dissolving the solid basic salt or by boiling an excess of litharge with a strong solution of neutral lead acetate.

† Prepared as follows: Shake powdered commercial alum with water at ordinary temperature until a saturated solution is obtained. Set aside a little of the solution, and to the residue add ammonia, little by little, stirring between additions, until the mixture is alkaline to litmus paper. Then drop in additions of the portion left aside, until the mixture is just acid to litmus paper. By this procedure a cream of aluminium hydroxide is obtained suspended in a solution of ammonium sulphate. This sulphate is advantageous when added after the basic acetate since it precipitates whatever excess of lead may be present.

sugars the use of alumina cream alone may be sufficient for clarification. Make up to volume with distilled water,* shake well and then pour the whole solution, or as much as practicable, on a dry filter. Reject the first 20 or 30 c.c. of filtrate and then polarize the remainder as already described for the pure sugar solution The average reading of the Ventzke scale, corrected for the deviation of the zero-point, is reported as "polarization."

Notes and Precautions. — Care must be taken to avoid the following errors due to manipulation; (1) change in moisture content of sample during weighing, (2) change in volume of solution due to fluctuations of temperature, (3) imperfect mixing of solution after diluting to volume in the graduated flask, (4) evaporation during filtration, (5) too great compression of cover glasses in closing the polariscope tube.

Clarification is very important. All proteids are lævoratory and must be entirely removed. The solution must be free from turbidity, but not necessarily free from color. Only so much of the clarifying agents should be used as is necessary to free the solution from optically active impurities and from turbidity. Any excess increases the error due to the presence of precipitate when the solution is diluted to volume. The volume occupied by the precipitate varies between 0.05 and 1.0 c.c. for ordinary raw sugars. It can be determined by Scheiber's method of double dilution † in which a duplicate determination is made in a flask of twice the volume, or by determining the weight and density of the precipitate as recommended by Sachs.† The latter method is preferred by Wiechmann § and Horne || each of whom determined the volume of the precipitate for a number of raw sugars from different localities. Horne has found (*loc. cit.*) that the error can be almost entirely avoided by clarifying with anhydrous basic acetate after the sugar solution has been diluted to volume.

Regulations of the International Commission.

The following resolutions ¶ adopted by the International Commission for the Unification of Sugar Analysis in 1900, have since been generally accepted.

* If frothing interferes at this point, add two or three drops of ether.

† *Ztschr. Vereins. Rübenzucker. Industrie*, 1875, **25**, 1054.

‡ *Ibid.*, 1880, **50**, 229. See also the paper by Horne.

§ *Ibid.*, 1903, [n. f.]**40**, 498; Abs. *Journ. Chem. Soc.*, 1903, **84**, ii, 699.

|| *Journ. Amer. Chem. Soc.*, 1904, **26**, 186.

¶ U. S. Dept. Agriculture, Bur. Chem., Bull. 73, p. 58. *Journ. Amer. Chem. Soc.*, 1901, **23**, 59–64.

1. In general, all sugar tests shall be made at 20° C.

2. The graduation of the saccharimeter shall be made at 20° C. Twenty-six grams of pure sugar, dissolved in water, and the volume made up to 100 metric cubic centimeters, or during the period of transition 26.048 grams of pure sugar in 100 Mohr cubic centimeters, all weighings to be made in air with brass weights, the completion of the volume and the polarizations to be made at 20° on an instrument graduated at 20°, should give an indication of 100 on the scale of the saccharimeter. For countries where temperatures are usually higher than 20°, it is permissible that saccharimeters be graduated at 30°, or any other suitable temperature, under the conditions specified above, providing that the analysis of the sugar be made at the same temperature — that is, that the volume be completed and the polarization made at the temperature specified.

3. Preparation of pure sugar: Purest commercial sugar is to be further purified in the following manner: A hot saturated aqueous solution is prepared and the sugar precipitated with absolute ethyl alcohol; the sugar is carefully spun in a small centrifugal machine and washed in the latter with absolute alcohol. The sugar thus obtained is re-dissolved in water, the saturated solution again precipitated with alcohol and washed as above. The product of the second crop of crystals is dried between blotting paper and preserved in glass vessels for use. The moisture still contained in the sugar is determined and taken into account when weighing the sugar which is to be used.

The committee further decided that central stations shall be designated in each country which are to be charged with the preparation and distribution of chemically pure sugar. Wherever this arrangement is not feasible, quartz plates, the values of which have been determined by means of chemically pure sugar, shall serve for the control of the saccharimeters.

The committee further decided that the above control of quartz plates by means of chemically pure sugar should, as a rule, apply only to the central stations which are to test the correctness of saccharimeters; for those who execute commercial analyses, the repeated control of the instruments is to be accomplished, now as before, by quartz plates.

4. In effecting the polarization of substances containing sugar, half-shade instruments, or triple field, only are to be employed.

5. During the observation the apparatus must be in a fixed position and so far removed from the source of light that the polarizing nicol is not warmed.

6. Sources of light may be gas, triple burner with metallic cylinder, lens and reflector; gas lamp with Auer (Welsbach) burner; electric lamp; petroleum duplex lamp; sodium light. Several readings are to be made and the mean thereof taken, but any one reading must not be neglected.

7. In making a polarization the whole normal weight for 100 cubic centimeters is to be used, or a multiple thereof for any corresponding volume.

8. As clarifying and decolorizing reagents there may be used: (*a*) subacetate of lead, (3 parts by weight of acetate of lead, one part by weight of oxide of lead, 10 parts by weight of water); (*b*) alumina cream; (*c*) concentrated solution of alum. Boneblack and decolorizing agents are to be excluded.

9. After bringing the solution exactly to the mark, at the proper temperature, and after wiping out the neck of the flask with filter paper, all of the well-shaken clarified sugar solution is poured upon a dry rapidly-acting filter. The first portions of the filtrate are to be rejected and the rest, which must be perfectly clear, used for polarization.

Relation of Polarization to Percentage of Sucrose.

In the absence of other active substances, the reading of the Ventzke scale as obtained above shows the percentage of sucrose in the sample. In commercial raw sugar the only other sugars likely to be present are dextrose and levulose. If the total amount of these reducing sugars, as shown by Fehling's solution, is small, the value of the sample is sufficiently indicated by the polarization, the invert-sugar, and the amounts of moisture and ash.

Since, however, the "reducing sugar" contains dextrose and levulose in unknown proportions, the determination of "reducing power" does not give the necessary data for estimating the percentage of sucrose in the sample. The percentage of sucrose can, however, be determined in the presence of a known mixture of dextrose and levulose by observing the change in rotation produced by hydrolysis. This is unaffected by the presences of monosaccharides since the latter cannot be hydrolyzed.

The following method is based on this principle.

CLERGET'S METHOD FOR SUCROSE.

A pure sucrose solution polarizing 100° on the Ventzke scale at a temperature of 20°, will, after hydrolysis, polarize — 33.6° on the same scale at the same temperature. It is this change of rotation from right to left which gives rise to the terms "inversion" for hydrolysis, and "invert-sugar" for the mixture of equal parts of dextrose and levulose produced. Since the lævorotary power of levulose, and hence of invert-sugar, decreases rapidly with increase of temperature the reading — 33.6° would be found only at 20°. An increase of 1° in temperature causes a decrease of 0.5 degree Ventzke in the lævorotation of the invert sugar, and at about 87.2° the reading becomes zero. The change in rotation produced by hydrolysis in pure sucrose solution is therefore, $143.6 - 0.5t$, in which t is the temperature at which the readings are taken.

To estimate the sucrose in an unknown sample, dissolve 26 grams, clarify, dilute to 100 c.c., filter and polarize as usual. Place 50 c.c. of the filtrate in a flask marked at 50 and 55 c.c., fill to the 55 c.c. mark with pure concentrated hydrochloric acid and mix well. Set the flask in water and heat until a thermometer suspended with the bulb at the center of the solution reads 68°, regulating the heat so that about 15 minutes is consumed in reaching the required temperature. Remove the flask, cool quickly, and polarize in a 220 mm. tube at exactly the temperature at which the first reading was taken. The change of rotation divided by that which pure sucrose would show under the same conditions, gives the percentage of sucrose in the sample. Or stating this in the form of an equation

$$\text{Sucrose} = \frac{a - b}{143.6 - 0.5t}$$

in which a is the first reading, b the second reading and t the temperature.

Notes. — In the above description the manipulation of Clerget and the figures found by Borntrager* and adopted by Wiley† have been followed. Landolt adopts other conditions requiring a different factor, 142.4 instead of 143.6. The temperature of each polarization must be carefully noted. Since the solution is increased one tenth in volume by the addition of hydrochloric acid, the sec-

* *Ztschr. Vereins Rubenzucker Ind.*, 1890, 876.

† Agricultural Analysis, Volume III., 108.

ond reading must be increased one tenth or made in a tube one tenth longer than that first used.

The Clerget principle can be applied to the determination of sucrose in the presence of any monosaccharide or mixture of monosaccharides. By the use of citric, in place of hydrochloric, acid, it can also be used for mixtures containing lactose.

Determination of Reducing Sugar.

Usually the reducing power of the raw sugar is determined volumetrically, as described in the preceding chapter, the results being calculated as percentage of invert sugar. For the determination dissolve 5 grams of the sample if dark, or 10 grams if light, dilute to 100 c.c. and filter through dry paper. If the preliminary test shows the solution to be too strong or too weak, prepare a fresh solution for the final determination. When the volumetric method is carefully carried out, the results are sufficiently exact for all ordinary work.* For the determination of very small amounts of invert-sugar the method introduced by Herzfeld,† and recommended by the International Commission,‡ is probably the most accurate.

Herzfeld's Gravimetric Method.

Dissolve 20 grams of sample in 80 c.c. of water, clarify with basic lead acetate and precipitate the excess of lead by sodium carbonate § (avoiding more than a slight excess) or by neutral potassium oxalate;‖ dilute to 100 c.c., mix thoroughly and filter through dry paper. The filtrate must be perfectly clear. In a beaker of 250 c.c. capacity, place 50 c.c. of the undiluted "mixed Fehling reagent" (see Fehling's volumetric method) and 50 c.c. of the clarified sugar solution; heat at such a rate that the mixture boils in about four minutes, and boil for exactly two minutes. Add 100 c.c. of cold, recently boiled distilled water, filter immediately, and find the amount of copper reduced as described under Defren's method in the preceding chapter. The following table shows the corresponding percentage of invert-sugar.

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* If a gravimetric method is preferred, use that of Meissl and Hiller, as adopted by the Official Agricultural Chemists: Bul. 46, Bur. Chem., U. S. Dept. Agriculture.

† *Ztschr. Vereins Rubenzucker Industrie*, 1886, 6.

‡ *Jour. Amer. Chem. Soc.*, 1901, **23**, 64.

§ Bull. 46, *loc. cit.*, p. 33.

‖ Sawyer: *Journ. Amer. Chem. Soc.*, 1904, **26**, 1631.

HERZFELD'S TABLE FOR THE DETERMINATION OF INVERT SUGAR IN MATERIALS CONTAINING 1 PER CENT. OR LESS OF INVERT SUGAR AND A HIGH PERCENTAGE OF SUCROSE.

Copper reduced by 10 grams of material. Milligrams.	Invert sugar. Per cent.	Copper reduced by 10 grams of material. Milligrams.	Invert sugar. Per cent.	Copper reduced by 10 grams of material. Milligrams.	Invert sugar. Per cent.
50	0.05	120	0.40	190	0.79
55	0.07	125	0.43	195	0.82
60	0.09	130	0.45	200	0.85
65	0.11	135	0.48	205	0.88
70	0.14	140	0.51	210	0.90
75	0.16	145	0.53	215	0.93
80	0.19	150	0.56	220	0.96
85	0.21	155	0.59	225	0.99
90	0.24	160	0.62	230	1.02
95	0.27	165	0.65	235	1.05
100	0.30	170	0.68	240	1.07
105	0.32	175	0.71	245	1.10
110	0.35	180	0.74		
115	0.38	185	0.76		

DETERMINATION OF MOISTURE AND ASH.

Dry about 2 grams of sample in a flat-bottomed platinum dish in the boiling water oven until the loss in weight on heating for one hour does not exceed 0.10 per cent. A perfectly constant weight cannot be expected if invert-sugar is present, since levulose is slowly decomposed by heating at 100° in the air. Calculate the loss of weight as moisture.

Moisten the residue with a few drops of concentrated sulphuric acid and burn to whiteness. Weigh; and report the result as "sulphated ash." The true ash is considered by some as nine-tenths and by others as four-fifths of the "sulphated ash."

OFFICIAL METHODS AND STANDARDS OF PURITY.

Methods of the Association of Official Agricultural Chemists: Bul. 46, Bur. Chem., U. S. Dept. Agriculture.

Regulations governing the sampling and classification of imported sugars and molasses: Treasury Department Document No. 2113.

German official methods: *Ztschr. Unters. Nahrungs- und Genussmittel*, 1903, 6, 1059; *Ztschr. anal. chem.*, 1903, 42 (Appendix to Nos. 9 and 10).

An act of Congress approved June 3, 1902, authorized the Secretary of Agriculture to establish standards of purity for food

products. The definitions and standards established for sugar and sugar products are as follows: *

1. *Sugar* is the product chemically known as sucrose (saccharose) chiefly obtained from sugar cane, sugar beets, sorghum, maple, or palm.

Standard sugar is white sugar containing at least ninety-nine and five-tenths (99.5) per cent. of sucrose.

2. *Granulated*, *loaf*, *cut*, *milled*, and *powdered sugars* are different forms of standard sugars.

3. *Maple sugar* is the solid product resulting from the evaporation of maple sap.

4. *Massecuite*, *melada*, *mush sugar*, and *concrete* are products obtained by evaporating the purified juice of a sugar-producing plant, or a solution of sugar, to a solid or semi-solid consistence in which the sugar chiefly exists in a crystalline state.

5. *Molasses* is the product left after separating the sugar from massecuite, melada, mush sugar, or concrete.

Standard molasses is molasses containing not more than twenty-five (25) per cent. of water nor more than five (5) per cent. of ash.

6. *Sirup* is the product obtained by purifying and evaporating the juice of a sugar-producing plant without removing any of the sugar.

7. *Sugar-cane sirup* is a sirup obtained by the evaporation of the juice of the sugar cane or by the solution of sugar-cane concrete.

8. *Sorghum sirup* is a sirup obtained by the evaporation of sorghum juice or by the solution of sorghum concrete.

9. *Maple sirup* is a sirup obtained by the evaporation of maple sap or by the solution of maple concrete.

10. *Sugar sirup* is a product obtained by dissolving sugar to the consistence of a sirup.

Standard sirup is a sirup containing not more than thirty (30) per cent. of water nor more than two and five-tenths (2.5) per cent. of ash.

DETERMINATION OF SUCROSE IN BEETS AND CANE.

Sucrose is the only sugar found in appreciable quantity in the fresh juice of healthy sugar beets. Sugar cane juice contains a small amount of reducing sugar which is usually considered to be invert-sugar, but which according to Wiley † is without influence upon polarized light. In either case therefore the polarization of

* U. S. Dept. of Agriculture, Office of the Secretary, Circular No. 10 (November 1903).

† Agricultural Analysis, Volume III., p. 234. The reducing substances of the original cane juice should not be confused with the invert-sugar produced by apart hydrolysis of sucrose, in the process of sugar manufacture.

a properly clarified sample is considered as showing the amount of sucrose present.

Beets after being thoroughly cleaned (the loss of weight in cleaning being determined and reported as "tare") are reduced to a fine pulp by rasping or grinding. This pulp is then treated in one of three ways (1) separating the insoluble matter by pressure and polarizing the juice, (2) extracting with alcohol, (3) extracting with water. The first method introduces errors from imperfect separation of the juice, the second is longer and more expensive than the third which is now generally used. If, however, the pulp be treated with water and filled to volume in a graduated flask as in the analysis of raw sugar it is very difficult to expel the air bubbles entirely from the mixture of pulp and water. The following method described by Sachs * avoids this inconvenience and has been found satisfactory for rapid work: Weigh 26 grams of the pulp in a beaker and add 177 c.c. of water containing 5 c.c. of the usual solution of basic lead acetate; shake or stir for three minutes; filter and polarize the filtrate. Twice the reading of the Ventzke scale is approximately the percentage of sucrose in the sample. This method assumes that 26 grams of beet pulp contain 23 c.c. of juice, making the total volume of liquid in the mixture 200 c.c. Many German sugar chemists hold that extraction with water gives high results because the beet contains substances other than sucrose which are soluble in water and rotate polarized light to the right. According to Sachs, however, these substances are pectin-like bodies and are completely precipitated by basic lead acetate. Trowbidge † also found that the results obtained by digestion in water were practically identical with those of the alcohol extraction method.

In sampling sugar cane for analysis, the canes are usually cut into thin oblique chips, "cosettes," by means of rotating knives. These cosettes may be further reduced by passing through a sausage cutter or a special shredding machine. It is not feasible, however, to reduce the cane to as fine a pulp as is obtained from sugar beets. For this reason more time and a higher temperature must be used to ensure complete extraction of the sucrose. According to Wiley, ‡ 26 grams of the chips of pulp are weighed into a

* Paper read before the Second International Congress of Applied Chemistry, Paris, 1896; quoted by Hiltner and Thatcher, *Journ. Amer. Chem. Soc.*, 1901, 23, 300.

† *Journ. Amer. Chem. Soc.*, 1901, 23, 222.

‡ Agricultural Analysis, Vol. III., p. 238.

flask graduated at 102.6 c.c., this graduation being based on the assumption that the cane contains ten per cent. of insoluble matter of a specific gravity about equal to that of the solution. The flask is nearly filled with water, and warmed on a water-bath for one hour with frequent shaking; then filled a little above the mark and warmed for ten minutes longer with frequent shaking. The flask is now cooled, the volume adjusted if necessary and the liquid filtered through dry paper. Fifty c.c. of filtrate are collected in a 55c.c. flask, clarified with basic acetate, filled to the mark, shaken, filtered, and the filtrate polarized in a 220 mm. tube.

For further information on the analysis of sugar beets and sugar cane, the following books and papers may be consulted:

Wiley: Agricultural Analysis, Vol. III., Part III.

Spencer: Handbook for Beet Sugar Chemists. Handbook for Sugar Manufacturers.

Lippmann and Pulvermacher: Lunge's Chemisch-technische Untersuchungsmethoden.

Frühling and Schultz: Anleitung zur Untersuchung für die Zuckerindustrie.

Trowbridge: Notes on Sugar Beets, *Journ. Amer. Chem. Soc.*, 1901, 23, 216.

Hiltner and Thatcher: An Improved Method for the Rapid Estimation of Sugar in Beets, *Journ. Amer. Chem. Soc.*, 1901, 23, 299, 863.

COMMERCIAL GLUCOSE.

Official Definitions and Standards of Purity. *

1. *Starch sugar or grape sugar* is the solid product obtained by hydrolyzing starch or a starch-containing substance until the greater part of the starch is converted into dextrose. Starch sugar or grape sugar appears in commerce in two forms, anhydrous and hydrous. In the former the sugar is crystallized without, in the latter with, water of crystallization. The hydrous varieties are commonly known as 70 and 80 sugars; 70 sugar is also known as brewers' sugar, and 80 sugar as climax or acme sugar.

(*a*) *Standard 70 sugar or brewers' sugar* is hydrous starch sugar containing not less than 70 per cent. of dextrose and not more than 0.8 per cent. of ash.

* U. S. Dept. Agriculture, Office of the Secretary, Circular No. 10.

(*b*) *Standard 80 sugar, climax or acme sugar*, is hydrous starch sugar containing not less than 80 per cent. of dextrose and not more than 1.5 per cent. of ash.

(*c*) *Standard anhydrous grape sugar* is anhydrous grape sugar containing not less than 95 per cent. of dextrose without water of crystallization and not more than 0.8 per cent. of ash.

The ash of these standard products consists almost entirely of chlorides and sulphates of calcium and sodium.

2. *Glucose, mixing glucose, or confectioners' glucose* is a thick sirupy substance obtained by incompletely hydrolyzing starch or a starch-containing substance, decolorizing and evaporating the product. It is found in various degrees of concentration, ranging from 41 to 45 degrees Baumé.

Standard glucose, mixing glucose, confectioners' glucose is colorless glucose, varying in density between 41 and 45 degrees Baumé, at a temperature of 100 degrees F. It conforms in density, within these limits, to the degree Baumé it is claimed to show, and for a density of 41 degrees Baumé contains not more than 21 per cent. of water, and for a density of 45 degrees not more than 14 per cent. It contains on a basis of 41 degrees Baumé not more than 1 per cent. of ash, consisting chiefly of chlorides and sulphates of calcium and sodium.

3. *Glucose sirup or corn sirup* is glucose unmixed or mixed with sirup or molasses.

Standard glucose sirup or corn sirup is glucose sirup or corn sirup containing not more than 25 per cent of water nor more than 3 per cent. of ash.

Analysis by Wiley's Method.*

This method was devised for the analysis of mixtures resulting from incomplete hydrolysis of starch, and is based on the assumption that dextrose and maltose are oxidized to optically inactive products when heated with an alkaline solution of mercuric cyanide and that dextrin is unaffected by the treatment and shows a specific rotation of + 193.

Dissolve 10 grams of sample in 60 to 70 c.c. of water in a 100 c.c. flask; boil for 10 to 15 minutes to secure a normal rotation of the reducing sugars; cool, add some alumina cream if the solution

* *Chem. News*, 1882, 46, 175, Agricultural Analysis, Vol. III., pp. 286–293.

is not clear, and fill to the mark. After thorough mixing, filter and polarize in a 200 mm. tube. Calculate the result as apparent specific rotation of the original sample.

To 10 c.c. of the same filtrate add 50 c.c. of the cyanide solution* and boil for 3 to 5 minutes. Add hydrochloric acid to faint excess, when the brown color of the solution will disappear; cool, and dilute the solution to 100 c.c. Filter (through animal charcoal if necessary) and polarize in the same instrument as before, This result is calculated to apparent specific rotation as before, basing the calculation on the entire amount of the original substance.

Dilute 10 c.c. of the filtrate first obtained to 100 c.c. and determine the reducing power by Defren's method (preceding chapter), or by Allihn's method, as given under determination of starch. Calculate the reducing power as percentage of dextrose in the original sample.

Let P = the first polarization calculated as apparent specific rotation (due to dextrose, maltose and dextrin).

P' = the second polarization calculated as apparent specific rotation (due to dextrin).

R = the reducing power calculated as dextrose.

d = dextrose.

m = maltose.

d' = dextrin.

Assuming the reducing power of maltose to be 0.61 that of dextrose, and the value $[\alpha]_D$ to be respectively, dextrose, 53; maltose, 138; dextrin, 193:

$$P = 53d + 138m + 193d'.$$
$$P' = 193d'.$$
$$R = d + 0.61m.$$

Solve for d, m and d', to obtain the amounts of dextrose, maltose and dextrin in the original sample.

Analysis by Other Methods.

Several other methods for the analysis of commercial glucose have been proposed. Some of these do not provide for the esti-

* Prepared by dissolving 120 grams of mercuric cyanide in water, adding 120 grams of sodium hydroxide and diluting the solution to 1 liter.

mation of maltose, but attribute the entire reducing power to dextrose. Others, including that of Allen, assume that dextrin, maltose and dextrose are the only organic compounds present. The percentage of solids is usually estimated from the specific gravity, the ash determined and deducted. Assuming that the total percentage of dextrose, maltose and dextrin is now known, the amount of each can be found by one determination of the apparent specific rotation and a determination of the reducing power. For details of the methods consult Allen's Commercial Organic Analysis, Volume I. (third edition), pages 358–378, and the following papers:

Brown, Morris and Millar: Experimental Methods Employed in the Examination of the Products of Starch Hydrolysis, *Journ. Chem. Soc.*, 1897, 71, 72.

Rolfe and Defren: An Analytical Investigation of the Hydrolysis of Starch by Acid, *Journ. Amer. Chem. Soc.*, 1896, 18, 869.

Rolfe and Faxton: The Exact Estimation of Total Carbohydrates in Acid Hydrolized Starch Products, *Journ. Amer. Chem. Soc.*, 1897, 19, 698.

Hönig: Ueber Zusammensetzung und Untersuchung von Stärkesyrupen, *Ztschr. Unters. Nahr.-Genussm.*, 1902, 5, 641.

ABSTRACTS.

ANALYTICAL CHEMISTRY.

By E. WALLER.

Gelatinous Precipitates. Dittrich (*Ber.*, XXXVII., 1840). The recommendation is made to add finely pulped filter paper. Washing is much more complete, and ignition is more readily effected. The method is claimed to be of especial advantage when re-solution of the precipitate is necessary.

Cupels. (*C. News*, XC., 23.) A correspondent states that magnesia cupels for small buttons are *as good* (not better than) bone ash cupels, but where the buttons are large (as in bullion assays) they are unsuitable on account of the large but variable quantity of magnesia adhering most persistently to the base of the buttons.

New Indicator—for Boric acid, etc. Robin (*C. Rend.*, CXXXVIII., 1046). 10 gms. yellow mimosa flowers are heated to boiling in 200 c.c. of water; when cold 50 c.c. of alcohol are added, and after standing an hour the solution is filtered. Use 1 drop of this solution in every 10 c.c. of liquid titrated. Golden yellow with alkalies. Colorless with acid. Paper saturated with this solution when soaked in a solution containing B_2O_3 and dried turns red when wetted with solution of Na_2CO_3.

Ammonia and Amides. Effront (*Ber.*, XXXVII., 4290). By digesting at ordinary temperatures a solution containing NH_3 or an amide or amido compound with solution of bleaching powder, and determining the amount of "available chlorine" destroyed by the reaction, the N present may be accurately measured. The process is applicable to water examinations, and may also be adapted for the determination of proteids as well as NH_3 in a sample. The accuracy is stated to extend to 0.1 mg. of a proteid per litre.

The solutions used are: (1) Normal NaOH; (2) Solution of bleaching powder containing 1.5 to 2 per cent. "available chlorine." This solution, well stoppered up, and kept away from the light will not change its strength in 30 hours; (3) Arsenious solution (4.585 gm. As_2O_3 with 13 gms. Na_2CO_3 per litre) 1 c.c. = 0.5 mg. NH_3; (4) Standard I solution.

For the test add to 1 litre of distilled water 20 c.c. of normal NaOH, and 20 c.c. of the "bleach" solution; cork up, and allow to stand 2 to 3 hours. Meantime treat 1 litre of the water to be tested in the same manner. (A duplicate is recommended.) At the end of the period add to the distilled water lot, a slight excess of the arsenious solution, then 20 c.c. N/H_2SO_4 and 10 c.c. of saturated solution of $NaHCO_3$ and then titrate back with standard I solution. To the portions under test, add As_2O_3 in amount just sufficient to reduce all the "bleach" solution used, in other respects conducting the test as described. Assuming the formula of the bleaching compound to be $CaOCl_2$, the equation for the reaction

with NH_3 appears to be: $2NH_3 + 3CaO\,Cl_2 = 3CaCl_2 + 3N_2O + 2N$, Cl per 1 gm. NH_3 Calc. 6.258 found 6.55.

To determine proteids, evaporate a litre of the water down to one tourth of its bulk (which expels all NH_3) and subject the remainder to che test, which will give the N in proteids. For egg albumen or for .asein, the proportion of Cl reduced per gm. of N in the compound was found to be about 18.6 gm. For peptones the figure was found to be about 15.3 gm. Hence if the As_2O_3 solution is of a strength so that 1 c.c. = 0.5 mg. NH_3 1 c.c. = 0.4117 mg. ammoniacal N and = 0.21503 mg. proteid N of digestion products, and = 0.17418 mg. proteid N of natural albumens.

As the proteids act slowly 14 to 16 hours digestion should be allowed. 2 to 3 hours or even less, will serve for NH_3.

Lithium-qualitative. Benedict (*Am. Chem. Jour.*, XXXII., 480). Add a little NH_4OH, then about one tenth the volume of $N/5Na_2HPO_4$ solution; finally add alcohol sufficient to afford a permanent precipitate in the cold. Now on heating to boiling the precipitate, if consisting only of Na_2HPO_4, will dissolve. If Li is present, it not only remains insoluble, but increases. If the Li is small the solution first clears then clouds up again.

Lime in presence of Phosphoric Acid. Jarvinen (*Zts. Anal. Chem.*, XXXIV., 559). Usually some CaO remains in solution, and some P_2O_5 accompanies the precipitate. If, however, the solution (as free as possible from NH_4 salts) receives the addition of NH_4OH until a permanent precipitate forms and then HCl to just clear it, is poured gradually when boiling hot into a mixture of $(NH_4)_2C_2O_4$ and $H_2C_2O_4$ (say 10 c.c. $N/(NH_4)_2C_2O_4$ with 5 c.c. $2N/H_2C_2O_4$ in 50 c.c. H_2O) the precipitate separates clean in small crystals. Finally add gradually a 1 per cent. solution of NH_4OH until neutral. Then filter, etc., as usual.

Strontium — Microchemical detection. Autenrieth (*Ber.*, XXXVII., 3882). In a moderately concentrated neutral or alkaline solution, $SrCrO_4$ will separate after a short time in fasciulate bundles of needles which are quite characteristic when viewed under the microscope. $BaCrO_4$ separated in amorphous form, $CaCrO_4$ practically not at all. To apply the test to best advantage, obtain the members of the group as chlorides, evaporate and dry them, then extract repeatedly with absolute alcohol, and filter, $BaCl_2$ is left. Evaporate the alcohol off, take up with a few c.c. of water, and to a drop of the clear solution add a drop of K_2CrO_4 on a microscope slide — allow to stand a couple of minutes before examining through the lens. If Sr is present the characteristic bundles of needles will be seen, which at once dissolve when a drop of acetic acid is placed on the slide.

Magnesium colorimetric. Schreiner and Ferris (*J. Am. Chem. Soc.*, XXVI., 961). The method consists in precipitating as ammonia phosphate in the usual manner and then dissolving in HNO_3 and, on addition of molybdate, making a colorimetric estimation. When Na_2HPO_4 was used as a precipitant "discouragingly high" results were obtained, owing to the difficulty of completely washing the soda salt from the filter and precipitate. K_2HPO_4 as precipitant was found to work satisfactorily. The reagent was prepared by dissolving 17.4 gms. K_2HPO_4, 100 gms. NH_4Cl

and 50 c.c. strong NH_4OH(Gr 0.9) in 1 litre. The other reagents were: (1)$(NH_4)_2MoO_4$ 50 gms. per litre. (2) HNO_3 of sp.gr. (1.07). (3) Standard phosphate solution 0.5045 pure crystallized $Na_2HPO_4 12.H_2O$ with 100 c.c. of HNO_3 (gr. 1.07) in 1 litre 1 c.c. = 0.0001 P_2O_5 = 0.000342 Mg.; NHOH for washing 1 part (vol. ?) of Gr. 0.9 with 9 parts (vols. ?) water. The filter papers used should be free from SiO_2. (4) Standard colorimetric solution 10 cc. of Standard phosphate diluted to about 80 c.c., 9 c.c. of HNO_3 (2) and 8 c.c. $(NH_4)_2MoO_4$ (1) made up to 100 c.c., and allowed to stand 20 minutes before making comparisons.

Chromium — Colorimetric. Moulin (*Bull. Soc. Chem.*, XXXI., 295). The method is based on Cazeneuve's reaction — purple coloration resulting from the reaction between diphenyl carbazide acetate and chromates in acetic solution. Dissolve (over a water bath) 2 gms. diphenyl carbazide in a mixture of 100 c.c. (90 per cent.) alcohol and 10 c.c. acetic acid, cool and dilute to 200 c.c. with alcohol. 2 c.c. of this reagent is used for each reaction. The Cr solution may contain 0.05 to 0.50 gm. CrO_3 per litre. 0.25 to 0.5 gm. of the sample may be taken for the test. After obtaining the Cr in solution as chromate, neutralize with acetic and dilute to some known bulk (100 to 200 c.c.). A standard solution of chromate is, of course, necessary for purposes of comparison. Allow to stand 20 minutes after adding the dicarbazide (which should be in excess) before reading off.

Ferric Iron — Colorimetric. Pulsifer (*J. Am. Chem. Soc.*, XXVI., 967). In slightly acid solutions acetyl acetone affords a reddish tint with ferric compounds, which can be used for colorimetric estimations. The reaction is not quite so delicate as sulpho-cyanate. Under the most favorable conditions the sulpho-cyanate will detect 0.00000004 Fe, whereas the acetyl acetone will detect only 0.000003 Fe. The color, however, is less affected by temperature, light and other conditions.

Iron — Iodometric Estimation. Namias and Carcano (*Monit. Sci.*, XVIII., Apr., '04). $Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + I_2$ is the reaction by means of which it has been attempted to determine Fe, starting with it in the ferric form. An estimation of the free I would seem to give the measure of the Fe present. It appears that a reverse action readily occurs, restoring some Fe to ferric form It was found that the addition of chloroform to remove the free I from the aqueous solution avoided this difficulty if the mixture was well shaken and allowed to stand for several hours.

Iron and Chromium — Separation. Southerden (*Chem. News*, LXXXIX, 181). The process is not new, consisting of fusing with KNO_3 and $KHSO_4$, thus converting to soluble K_2CrO_4 and insoluble Fe_2O_3. The interesting feature is that it can be made in a test-tube without injury to the latter if the dried precipitate is mixed with KNO_3, the mass cautiously brought to fusion, and fragments of $KHSO_4$ dropped in. Even mineral chromite treated in this manner can readily be made to give up sufficient Cr to give decided indication in the water solution.

Bauxite Analysis. Taurel (*Am. Chim. Anal. Appl.*, IX., 323). Fuse 2 gms. of the mineral with 8 to 10 gms. of the $NaKCO_3$ mixture

until effervescence ceases. Cool — dissolve in water — add 20 cc. strong H_2SO_4 and evaporate to fumes. Dilute and filter off SiO_2. Dilute the filtrate to one liter, and run 100 cc. of the dilution gradually into a mixture of 10 cc. NH_4OH with 50 cc. water, boil — filter — wash with boiling water, redissolve the precipitate HCl, and reprecipitate with NH_4OH. To the solution containing the suspended precipitate add excess of formic acid, and 1 gm. Na_2SO_3 (or pass in SO_2 gas) and boil gently for an hour, which precipitates TiO_2. Then add citrate or tartrate to the extent of 8 or 10 times the amount of Al_2O_3 present, then excess of NH_4OH, and then $(NH_4)_2S$, which brings down Fe. If filtering is postponed until this point, the ignited precipitate will represent $Fe_2O_2 + TiO_2$.

Separating Iron from Zirconia. Von Knorre (*Zts. Angew. Chem.*, XVII., 641). In a solution of the chlorids containing $H_2C_2O_4$, strong acidification with HCl, heating to boiling and then adding nitroso-beta-napthol in acetic solution will completely precipitate Fe leaving the Zr entirely in the solution.

Separating Iron from Nickel and Cobalt. Field's method. Laby (*Chem. News,*) LXXXIX., 280). The solution of the metals as nitrates is evaporated to dryness on the water bath, water is added to the residue, and after heating to boiling an excess of PbO is introduced (at least six times as much as there is Fe present) filter and wash hot with addition of a little $Pb(NO_3)_2$ to the wash water. Pb may be removed from the filtrate by H_2SO_4. Separation of the Fe is complete and rapid. One per cent. or less of the Ni or Co may be retained by the precipitate.

Qualitative for Nickel and Cobalt. Benedict (*J. Am. Chem. Soc.*, XXVI., 695). To detect small amounts of Ni in presence of Co. Add excess of Na_2O_2 and heat to boiling — filter, wash until cold, then pour through the filter a cold saturated solution of $H_2C_2O_4$. Pour this through the filter three or four times. Then to this solution add a few drops of ferricyanide and then slight excess of Na_2O_2. Black $Ni_2(OH)_6$ is precipitated. Co remains on the original filter as hydrated peroxide.

To detect either one or both. Add to the solution NaOH (of about 5N strength) in excess and agitate for about half a minute. When Co only is present, the precipitate is momentarily blue, and changes almost immediately to pink. When Ni is present, this change of color is retarded — very materially so in case decided amounts of Ni are present.

Zinc in Cyanide Solutions. Cross (*J. Chem. Met. and Min. Soc. S. Afr.*, III., 165). 100 cc. of a working solution is treated at about 70° C. with excess of 5 per cent. Na_2S solution. After settling the precipitate of ZnS is filtered, and washed with hot water until all soluble sulphide is removed. The precipitate, paper and all, is then placed in a 150 cc. flask fitted with a cork having two holes; through one hole passes a short tube for vent with rubber tube and pinch cock, through the other the stem of a globe stop-cock tube, an excess of N/10 iodine is poured onto the precipitate, and the cork then adjusted. 100 c.c. of very dilute HCl is then put into the globe, and slowly run into the flask, the vent tube being manipulated so as to allow the air to escape. When all is in, close pinch cock and stop cock and shake thoroughly. The solution is then titrated back with N/10 $Na_2S_2O_3$. The amount of $Na_2S_2O_3$ solu-

tion rendered unnecessary by action of the H_2S from the ZnS multiplied by 0.00325 gives the amount of Zn present.

Bismuth Qualitative. Reichard (*Chem. Ztg.*, XXVIII., 1024.) Brucine when added in solid form or concentrated solution containing Bi gives a red coloration, permanent when the reagent is in excess, which color becomes more intense by heating. The coloration with HNO_3 fades to yellow on heating. Sb will give a similar coloration when hot, but no color in the cold. To obtain the reaction with basic Bi salts, a trace of HCl should be added.

Bismuth in Minute Amounts in Copper and its Ores. Cloud (*J. S. C. I.*, XXIII., 523.) A colorimetric method is based on the fact that addition of KI to a solution containing Pb and small amounts of Bi affords a precipitate with an orange or red tint, the depth of tint being proportionate to the amount of Bi present. Qualitatively 0.001 gm. Bi can be detected.

The solutions required are: 1 standard Bi solution. Dissolve pure Bi_2O_3 in HNO_3 sufficient to hold it in solution when diluted until 1 c.c. = 0.0001 gm. Bi.

2. $Pb(NO_3)_2$. Dissolve 6 gms. pure Pb in HNO_3, evaporate off excess of acid, etc., and dilute to 1 liter.

3. KI 30 gms in 4 liters.

For metallic Cu, dissolve a weighed amount in HNO_3, and add Na_2CO_3 until a small permanent precipitate remains. Allow to stand some hours with stirring. Finally filter. Without washing dissolve in HCl and use this solution for the H_2S treatment as below. If much Pb is present treat as described for ores.

For ores dissolve in HNO_3 and H_2SO_4, evaporate to fumes. Add water and a little HCl, and after filtering pass H_2S. Dissolve the sulphides in HNO_3 and make up to 250 c.c. To half of this solution add 5 c.c, of the $Pb(NO_3)_2$ solution, agitate well, neutralize with NH_4OH and add $(NH_4)_2CO_3$, followed by NH_4OH to keep the Cu in solution. Digest on the water bath and wash with NH_4OH water until all Cu is removed. Dissolve the precipitate in HNO_3, evaporate to the crystallization point, then dilute up with weak HNO_3 to 25 c.c. — add 25 c.c. of the KI solution and compare with tubes (Nessler) made up with varying amounts of the standard Bi solution together with 1 c.c. HNO_3, 5 c.c. of $Pb(NO_3)_2$ 25 c.c. of KI and water to bring it up to 50 c.c. Read off after standing fifteen to twenty minutes.

Antimony Determinations. Gutbier and Brunner (*Zts. Angew. Chem.*, XVII., 1137). An examination of the estimation of Sb gravimetrically as Sb_2S_3 and as Sb_2O_4. Both methods are found to be accurate with proper precautions. Estimation as Sb_2O_4 seems to require the greatest precaution. The method prescribed by Brunck should be followed. As is first removed by distillation in an HCl solution in either case. To separate Sb_2S_3 it was found best to saturate (with gaseous H_2S) the acid solution from the distillation, kept standing on a boiling water bath, and then to add gradually an equal bulk of hot water. Under these conditions the precipitate separates readily in flocks without adhering to the sides. The solution is finally brought to a vigorous boil before filtering. For determination as Sb_2S_3 the filtering is performed in a

specially devised filter tube (with asbestos), capable of afterward being heated inside another in an atmosphere of CO_2, which is done after thorough drying at 105°. The precaution not to fill the tube too high when filtering is especially insisted on. Heating uniformly and not heating too highly are also important.

In the oxidation method (to get Sb_2O_4) the last portions of Sb_2S_3 should be removed from the filter by a little $(NH_4)_2S$ solution. After drying on a water bath the precipitate was moistened with red fuming HNO_3 and heated to dryness. After this, oxidation under a bell glass, as directed by P. Jaunasch, was performed, the crucible being supported on a glass triangle over a capsule of fuming nitric in a warm place in sunlight. The final oxidation was effected in the crucible sunk as far as possible through a hole in a sheet of iron, cut to fit so that the products of combustion should not reach the contents of the crucible, and the flame of a burner applied.

Tin, or Mixtures of Tin and Antimony. Angenot (*Zts. Angew. Chem.*, XVII., 1275). Fusion with Na_2O_2 affords the Sn in soluble form from which it may be precipitated by acidifying with H_2SO_4 and boiling. If Sb is present the solution of the melt, after filtering, is treated with alcohol in proportion sufficient to give 1 vol. alcohol to 2 vols. water and allowed to stand half an hour. Sodium pyroantimoniate remains insoluble. The separation is quantitative.

Lead in Brass and Bronze. Ericson (*J. Am. Chem. Soc.*, XXVI., 1135). The method depends upon obtaining the metal as PbO_2 by use of persulphate, then adding a known amount of H_2O_2 solution which causes reduction of the PbO_2, and then titrating the excess of H_2O_2 with standard $K_2Mn_2O_8$.

The solutions necessary are: H_2O_2 solution (for low percentages of Pb), 15 c.c. of U. S. P. H_2O_2 solution, 900 c.c. water, and 50 c.c. HNO_3. Permanganate 1.139 gms. (theoretically 1.1324) in 1 litre standardize with pure iron wire. 1 c.c. should = 0.002 Fe or = 0.00384 Pb. According to the equation it should = 0.003702 Pb but experiment has shown that the above empirical figure is the correct one.

Dissolve 1 gm. of the drillings in 15 c.c. HNO_3 (sp. gr. 1.28) boil slowly down to 6 c.c., add 100 c.c. water, boil and settle. Filter, wash with 2 per cent. HNO_3 dry, ignite and weigh SnO_2. To the filtrate add 25 c.c. strong NH_4OH and gradually 3 to 4 gms. solid $(NH_4)_2S_2O_7$, boil 5 minutes settle and filter. Wash first with dilute NH_4OH (1:5) then four or five times with hot water. Place filter and precipitate in the beaker in which precipitation was made, stir and add 25 c.c. of H_2O_2 solution. When all or nearly all the dark particles have disappeared, add 20 c.c. HNO_3 (gr. 1.28) and 150 c.c. water, stir well and titrate with the standard permanganate, titrating also a blank of 25 c.c. of the H_2O_2 solution mixed with the same amounts of acid and water. By rendering this solution ammoniacal, all Pb and Fe may be precipitated out and from the precipitate the Fe may be dissolved out, and determined.

Tin in Tin Plate. Angenot (*Zts. Angew. Chem.*, XVII., 521). Cut into pieces not over 1 cm. on a side. Weigh off 3 to 4 gms. Place in an iron crucible, and add twice its weight of Na_2O_2. Heat up gradually, finally to full fusion. In the course of about ten minutes it can be seen

that the Sn is entirely removed from the fragments. Cool, put into a covered beaker, add 100 c.c. water, to dissolve the stannate, make up to 250 c.c. mix, and filter off 200 c.c. Add H_2SO_4 (1 vol. to 2 vols. water) until slightly acid, boil five minutes, then filter, wash, ignite and weigh as SnO_2.

Colorimetric for Gold in Cyanide Solutions. Prister (*J. Chem. Met. and Min. Soc. S. Afr.*, IV., 235). The purple of Cassius test is used. A standard solution of Au is made by dissolving a weighed quantity in aqua regia, and taking portions which are diluted up with a mixture of glycerin and KOH (or NaOH) solution. According to richness take 100 to 200 c.c. of the cyanide solution, acidify with HCl, and boil a couple of minutes to decompose free cyanide. Then add a slight excess of Cu solution (made by dissolving 1 part cryst. $CuSO_4$ in 10 parts H_2O adding 2 parts NaCl and Cu turnings then boiling 10 minutes and on cooling adding some acetic acid). This affords $KAuCy_2$. Test for excess of Cu by spot test with ferrocyanide. Add a few drops of 1 to 2 per cent. Na_2S solution (not too much). Boil 5 minutes, let settle, and decant through a filter. Treat the precipitate (in the beaker and on the filter) with 2.5 or 3 c.c. of a 3 to 5 per cent. solution of KCy. Adding a few drops of KOH facilitates the solution of the precipitate. To the solution (clear or turbid) add 1 to 2 gms. Zn dust, and warm (30 to 40°) for about 30 minutes. Filter by decanting through the same filter. The residue is, or may be Au + Ag + Cu + Zn. Dissolve off the Zn by dilute HCl. Dissolve the residue in 10 c c. aqua regia, passing the solution three or four times through the filter. Dilute to 20 c.c. add $SnCl_2$ solution and compare with the standards, treated in a similar manner. The accuracy obtainable is claimed to be superior to fire assay.

Separation of Gold from Platinum. Willstaetter (*Ber.*, XXXVI., 1830). $AuCl_3$ is soluble in ether, while $PtCl_4$ or H_2PtCl_6 is not. Three successive treatments with ether will serve to effect a complete separation of the compounds from one another.

Assays of Alloys of Platinum, Gold and Silver. Hollard and Bertiaux (*Bull. Soc. Chim.*, XXXI., 1031). The method usually used consists in cupelling with Pb, affording the mixture of Pt, Au and Ag, adding silver and lead-cupelling, dissolving out Ag by H_2SO_6 and weighing Pt + Au. On a fresh portion repeated fusion with Ag and treatment with HNO_3 by which means Pt is eventually entirely removed leaving Au only. An examination of the method with known weights of the metals in different proportion shows that the process gives low results on Au, results essentially accurate for the mixture of Pt + Au, high results for Pt and also for Ag.

Palladium. Erdman and Makowka (*Ber.*, XXXVII., 2694). The separation of Pd by use of hydrazin elaborated by Jaunasch and his fellow workers is much more troublesome than that with acetylen in HCl solution. With acetylen the separation occurs completely and readily. Treating with the gas for fifteen minutes in an Erlenmeyer flask is sufficient. The precipitated acetylide is readily filtered and washed, and by ignition converted to metal for weighing. When mixed with Cu the separation is complete and adding NH_4OH to the filtrate, then hydroxylamin chloride

and passing acetylen for five minutes precipitates the Cu which can be oxidized by HNO_3 and weighed as CuO.

Thorium in Monazite, etc. Neish (*J. Am. Chem. Soc.*, XXVI., 780). In neutral solution metanitrobenzoic acid — $H.C_6H_4NO_2CO_2$ — was found to precipitate Th completely. Some small amounts of Ce, La, etc., contaminated the precipitate, but on redissolving in HNO_3, and neutralizing closely with NH_4OH by aid of methyl orange indicator the third precipitation affords the pure Th $(C_6H_4NO_2CO_2)_4$ containing 25.93 per cent. Th. Warming for fifteen minutes at 60° to 80° C. causes the bulky white precipitate to separate in flocks resembling AgCl. By careful ignition it yields pure ThO_2, the volatile constituents burning with a smoky flame. When dried it is electrified and is radioactive.

Two gms. of the finely pulverized monazite are treated in a porcelain crucible with 10 to 15 c.c. of concentrated H_2SO_4 at a temperature sufficiently high to cause fumes of SO_3. Three hours' digestion was found to suffice. The cooled solution is then poured drop by drop into about 600 c.c. of ice water. After filtering, the solution is heated to boiling, and a cold saturated solution of $H_2C_2O_4$ heated to boiling is gradually added with stirring. When cool, the precipitate of oxalates is filtered off, converted to hydroxides by boiling with 10 to 15 gms. KOH, in concentrated solution — after dilution to 300 c.c. this is filtered and washed free from alkali. The hydroxides are then dissolved in hot dilute HNO_3 and this solution evaporated, and re-evaporated until all free HNO_3 is expelled. The solution of these nitrates is then diluted to 500 or 600 c.c. and 150 to 250 c.c. of a cold saturated solution of the reagent added. The management of the precipitation, re-solution, etc., has been sketched out above. Instead of reprecipitation of the meta-nitro-benzoate by NH_4OH, the solution of the precipitate in HNO_3 may be precipitated by use of a slight excess of KOH, to obtain hydroxide, which is dissolved in HNO_3 and treated de novo. This mode of operating, though longer, is more easily carried out.

Lanthanum Reactions. Orlow (*Chem. Ztg. Rep.*, XXXIII., 36). Iodine reacts upon the basic salt resulting from the action of NH_4OH on lanthanum acetate, affording a blue color.

Vanadium — Separation from Iron and Alumina. Glasman (*Chem. Centr.*, 1904, 1537). Addition of H_2SO_4 and KI reduces the V_2O_5 to V_2O_3. The free I is removed by SO_2. Then, on neutralizing with KOH, addition of a mixture of KI and KIO_3 precipitates $Fe_2(OH)_6$ and $Al_2(OH)_6$, one or both, thus:

$$Fe_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = Fe_2(OH)_6 + 3K_2SO_4 + 3I_2$$

The free I is destroyed by $Na_2S_2O_3$ then filter. V remains in solution.

Vanadium and Chromium in the Same Solution. Campagne (*Bull. Sc. Chem.*, XXXII, 962). The solution, from which Fe has been removed, is evaporated several times with HCl to reduce them to $VOCl_2$ and Cr_2Cl_6. Then add excess of H_2SO_4 and evaporate to fumes to convert to sulphates, dilute largely and titrate cold with standard $K_2Mn_2O_8$. Under these conditions only the V salt is oxidized, and the amount may be determined. Then add an excess of $K_2Mn_2O_8$ and boil vigorously when the Cr is converted to chromate. Excess of $K_2Mn_2O_8$ is removed

by boiling with addition of a few scraps of filter paper. Filter; then, by adding a known amount of $Fe(NH_4)_2(SO_4)_2$ and titrating with $K_2Mn_2O_8$, the Cr may be determined.

Separation of Selenium from Tellurium. Pellini (*Gaz. Chem. Ital.*, XXXIII., 515). After acidifying slightly with HCl, add a cold saturated solution of $NH_4HC_4H_4O_6$, then hydrazine sulphate. Se alone is precipitated, the Fe remaining in solution.

Chlorides in Mossy or Peaty Waters. Tatlock and Thomson (*J. S. C. I.*, XXIII., 429). To remove the color, which ordinarily interferes with the titration by standard $AgNO_3$, the authors add a little calcined magnesia and filter before measuring off for titration. If ferrous compounds are present, it may be found necessary to add a few drops of H_2O_2 before using the MgO.

Chlorides in Presence of Bromide. Jones (*Chem. News*, LXXXIX., 229). Cold NH_4HCO_3 solution in contact with the Ag salts for a few minutes dissolves almost exclusively the AgCl. On acidifying the clear solution with HNO_3, the AgCl is made to separate. A slight turbidity may be due to traces of bromide. Test by taking a portion of the turbid liquid and adding a slight excess of the NH_4HCO_3 solution. A turbidity caused by AgBr is slow to disappear. If due to AgCl it clears mmediately.

Chloric Acid. Hendrixson (*Am. Chem. Jour.*, XXXII., 242). It has been found that metallic iron completely reduces $HClO_3$ to chloride. The method consists in treating a solution of $HClO_3$ or the chlorate in a small flask at the ordinary temperature with about 50 c.c. H_2SO_4 (10 per cent. strength) and excess of iron (such as is used for standardizing permanganate). After standing an hour, when the solution should have passed through yellowish to green, HNO_3 is added until FeO is oxidized, and the solution is titrated with N/20 $AgNO_3$ by the Volhard method.

Perchlorate in Commercial Sodium Nitrate. Lemaitre (*Monit. Sci.*, XVIII., Apr., 1904). On fusing cautiously a mixture of 5 gms. of the sample with 3 gms. Na_2SO_3, the perchlorate is converted to chloride. On cooling, and dissolving in water, and bringing to a boil — a large excess of a boiling solution of $Ba(NO_3)_2$ is added (200 c.c. of a 4 per cent. solution). Filter after settling, add 8.2 c.c. normal NaOH, then 1.2 gms. persulphate — boil and filter. Neutralize the filtrate with acetic and titrate with standard $AgNO_3$. Chlorine as chloride and iodine in any compound in which it may be present, may be determined in separate portions of the sample, and the results with the $AgNO_3$ titration corrected accordingly.

Bromides and Iodides in Springs and Streams. Orlow (*Chem. Ztg. Rep.*, XXVIII., 36). Wrap up some freshly precipitated AgCl in hardened filter paper, and immerse for 24 hours in the spring or stream. When Br or I are present, a portion of the AgCl will be converted to AgBr or AgI.

Iodine in Presence of Bromine and Chlorine. Thilo (*Chem. Ztg.*, XXVIII., 866). The solution is titrated slowly with stirring, with N/10 $AgNO_3$ until a drop gives no dark spot on a paper impregnated with a weak solution of PdCl. The solution may afterward be used for determination of Br and Cl.

Sulphur — Commercial. Ceruti (*Boll. Chim. farm.*, 1904, 421). Extract 1 to 2 gms. of the sample on a weighed filter with aniline (b.pt. 180 to 185°C. at a temperature of 120° to 130°C. Wash with alcohol, dry and weigh. Neutralize the filtrate with HCl, which precipitates the pure S. After washing this is dried over H_2SO_4 and weighed.

Sulphur in Iron and Steel — New method. Pulsifer (*Iron and Steel Mag.*, per C.N, XC., 230). The method consists in dissolving the drillings is $HClO_3$ with addition of HF followed up by HCl, fusing the residue with Na_2O_2 dissolving, etc., and in the united solutions precipitating with $BaCl_2$.

2.5 gms. of the sample are moistened with water, in a 250 c.c. Jena beaker. Then 20 c.c. of $HClO_3$ and a very little HF are added. Solution takes place rapidly. When the action subsides add 5 c.c. strong HCl, cover, and boil enough to wash the particles down from the sides of the beaker. Then filter, using suction, and wash two or three times with as little water as possible, and suck dry. Boil down the filtrate after adding 20 c.c. strong HCl until it is syrupy and about 10 c.c. in bulk.

Place the moist filter paper in a small Ni crucible, cover it with Na_2O_2 and holding the cover down with the tongs apply a strong flame. The fusion takes but a few seconds. As soon as may be, soak out with 50 c.c. of water, add HCl in excess, and filter into the main portion. The bulk should now be about 100 c c. and it is now ready for the $BaCl_2$ solution. These operations can all be carried through in about 20 minutes. The test analyses by this method compare fairly well with results by other methods.

Sulphur in Calcium Carbide. Lidholm (*Zts. Angew. Chem.*, XVII., 558). 3 gms. of the pulverized sample is mixed in a porcelain crucible with five times its weight of a mixture of $KNaCO_3$ with two parts NH_4Cl, and heated (covered) over a spirit lamp to fusion. By moving about with the tongs the carbide can easily be decomposed. The fusion takes place at a comparatively low temperature. After about 5 minutes of fusion, the mass is poured out upon a marble slab, and when cooled, broken up and placed in a flask from which by treatment with HCl the H_2S may be passed into $Cd(C_2H_3O_2)_2$ solution, or a solution of mixed Cd and Zn acetates. On adding an acidified solution of $CuSO_4$ to that containing the suspended sulphides, all S is converted to CuS which can be filtered off, washed, etc., ignited to CuO and weighed.

Persulphates. Wolff and Wolffenstein (*Ber.*, XXXVII., 3213). The reagent used is a cold saturated aqueous solution of SO_2 containing some $BaCl_2$. Mixing with paper pulp and filtering affords a clear solution. Place a weighed quantity of the persulphate in an Erlenmeyer flask provided with a Bunsen valve, add HCl, and then the reagent in excess, and heat until no more odor of SO_2 is perceptible. Then filter and weigh the $BaSO_4$ in the usual manner.

The reaction is: $H_2S_2O_8 + SO_2 + 2H_2O = 3H_2SO_4$.

Consequently two thirds of the sulphur thus found must be calculated as persulphate.

Phosphorus in Solutions. Christomanos (*Zts. Anorg. Chem.*, XLI., 305). An ether solution of the P is agitated for some minutes with an

excess of 10 per cent. $Cu(NO_3)_2$ solution. Copper phosphides of varying composition will separate as a black precipitate. After expelling the ether Br is added which converts the phosphide into phosphate. The Cu is separated by H_2S and the phosphate determined in the usual manner.

Hydrofluoric Acid Titration. Katz (*Chem. Ztg.*, XXVIII., 356, *ib.*, 387). If HF only is present, it may be titrated directly with standard alkali, using phenol phthalein as indicator. If hydrofluosilicic acid is present, that acid gradually decomposes, affording six equivalents of HF, giving an end reaction only when this has been effected. Addition of 50 per cent. of alcohol will prevent this decomposition. 10 gms. of the acid are therefore titrated in a platinum dish at boiling temperature with N/2KOH. This gives all the F present in terms of HF. Then weigh out 10 gms. of the acid in a paraffined beaker, add 100 c.c. of 60 per cent. alcohol and titrate with N/2KOH. This gives $HF + H_2SiF_6$ (dibasic) by calculation, the relative amounts are estimated.

Silicon in Iron and Steel. Thiel (*Zts. Anal. Chem.*, XXXIV., 552). In Drown's method, the solution bumps dangerously as the solution becomes concentrated (by naked heat). This can be avoided by making up the solution thus: 1 litre water, 1 litre conc. H_2SO_4, 1 litre. conc. HNO_3 and 1 litre of NH_4Cl solution (240 gms. of the salt). Use 50 to 70 c.c. of this mixture for 1 to 2 gms. of the sample.

Boric Acid. Schaak (*J. S. C. I.*, XXIII., 699). A brief review of the different methods proposed is given. Three methods are described: I. Adding standard acid until the solution reacts acid to methyl orange boiling out CO_2, cooling, rendering neutral to methyl orange, adding full one third the volume of glycerol, and titrating the B_2O_3 with standard acid to neutrality with phenolphthalein.

When Al or Fe are present the results are inaccurate, in which case II is used. This consists in dissolving with HCl, and boiling with reflux condenser. After cooling, the solution is made up to some definite volume, and an aliquot portion filtered off. To this after nearly neutralizing to methyl orange is added $BaCO_3$ in excess, and the mixture heated 30 minutes on the water bath when it is filtered, after cooling and making up to definite volume. Under these conditions, the B_2O_3 remains free in the solution and in aliquot portions of the solution may be titrated by adding glycerol, etc., as before.

III. Distillation with methyl alchol. Any free mineral in the distillate may be neutralized (with aid of methyl orange). The substance is made into a paste with conc. H_2SO_4 and gently warmed to expel CO_2. This mixing is affected in the distilling flask. Then 20 times as much methyl alcohol as H_2SO_4 is added and the flask closed with a cork carrying three tubes. One connects with the receiver, which contains about 60 c.c. of water, the delivery tube dipping below the surface. The receiver connects with the outside air only through a Mohr bulb. Another tube delivers methyl alcohol vapor near the bottom of the flask. The third tube delivers the liquid methyl alcohol required. About 30 minutes suffice for a distillation. The distillate is treated as in I. or II. for titration of the B_2O_3.

Boric Acid in Cider, Fruits, etc. Allen and Tankard. (*Analyst*, XXIX., 301. Qualitatively this may be detected by the turmeric paper test

on the solution of the ash after careful incineration. B_2O_3 has been detected as a natural constituent in a variety of fruits. A summary of the references on this subject is given. The titration in presence of glycerin is incorrect when phosphates are in the solution. The method of avoiding this difficulty pursued by the authors depends on the moderate solubility of Ca_3BO_3 in water. One hundred c.c. of a liquid (such as cider) or 50 gms. of a sliced fruit receive the addition of a few c.c. of strong $CaCl_2$ solution. The mass is then dried and heated to charring, boiled with 150 c.c. of water, filtered, then calcined and again boiled with water. A third treatment is recommended, in the extract from which, by qualitative test, one can prove whether all B_2O_3 is extracted. The solutions are united, evaporated down to 25 or 30 c.c. and the glycerin titration test applied, *i. e.*, render neutral to methyl orange, add an equal volume of glycerin, and titrate the free B_2O_3 with N/20 NaOH and phenolphthalein indicator. One c.c. of N/20 NaOH = 0.00175 gm. B_2O_3, 0.0013 gm. H_3BO_3 or 0.004775 gm. (crystallized borax) $Na_2B_4O_7.10H_2O$.

For the distillation test with methyl alcohol the solution is obtained in essentially the same manner as above, carbonizing, washing, incineration, etc. Six successive distillations with methyl alcohol, 10 c.c. each time, are necessary, the flask being allowed to cool down to ordinary temperature each time. The receiver should contain water only (no NaOH) into which the delivery tube dips.

Nitrogen in Iron and Steel. Braune (*Oesterr. Zts. Berg-Hütt*, LII., 491). Fit a capacious Erlenmeyer flask with a cork carrying a funnel tube and a tube connecting with a condenser. Introduce 250 c.c. of water and 20 c.c. strong NaOH solution. Dissolve 1 gm. of the sample in 10 c.c. of the HCl free from N compounds, and filter the solution slowly into the boiling alkali solution Determine NH_3 in the distillate by Nesslerization.

Organic Nitrogen by use of Sodium Peroxide. Von Konek and Zöhls (*Zts. Angew. Chem.*, XVII., 1093). The method was devised for the determination of N in flours and meal, though it has been found applicable to some other substances containing N (aliphatic compounds containing amin — or amido N). It consists in deflagrating about 0.5 gm. of the substance after intimately mixing with 12 gms. Na_2O_2 in a nickel-lined steel cylinder, to which is afterward added 5 to 6 gms. Na_2O_2 and about 1 gm. of a persulphate-tartaric mixture (2 parts $K_2S_2O_8$ with 1 part $H_2C_4H_4O_6$). The materials must be all as dry as possible (dried a few hours in the air bath). After mixing the charge, screw down the cover, and fire by a red hot iron wire. The N is by this means converted to $NaNO_3$, and after dissolving out is converted by boiling with the Devarda alloy Al + Cu (vid QUARTERLY) to NH_3 and determined as such in the distillate.

Kjeldahl Method. Sherman and Falk (*J. Am. Chem. Soc.*, XXVI., 1469). Decolorization of the H_2SO_4 cannot be taken as an indication of the complete conversion of the N of the sample to NH_3, still less so when $KHSO_4$ has not been used or the decolorization occurs quickly. The results of the experiments of the authors indicate that both metallic Hg and $KHSO_4$ should be added (as recommend by Dyer) and that the

boiling should be continued for full half an hour after decolorization occurs—an hour or more, if decolorization ensues very soon.

Nitrates and Nitrites in Waters. Tatlock and Thomson (*J. S. C. L.*, XXIII., 429). The phenol sulphonic method is regarded as the most handy and reliable. The amount of chloride present having been previously ascertained, the necessary amount of finely divided pure Ag_2O is added to 100 to 200 c.c. of the water, and the mixture well agitated. Much excess of Ag_2O gives low results. Then about 0.1 gr. of $Al_2(SO_4)_3$ is dissolved in the sample, and after that some calcined magnesia is added, and the whole filtered after agitation. (Without the Al compound the AgCl cannot be readily filtered off completely.) In a measured portion of the clear filtrate (50 or 100 c.c.) the usual phenol sulphonic test is applied. Nitrites if present scarcely at all affect the result for nitrates, but if to a portion of the clarified filtrate is added some H_2O_2, and the whole evaporated to dryness, the nitrites are converted to nitrates, when the difference of the two results by phenol sulphonic test will afford the measure of the nitrites.

Hydroxylamine. Simon (*C. Rend.*, CXXXVII). Add a few drops of dilute solution of sodium nitroprusside, then a slight excess of alkali, and boil. The color of the solution changes from yellow to deep cherry red if even small amounts of hydroxylamine are present.

Cyanide—Volumetric. McDowall (*Ch. News*, LXXXIX, 229). The standard solution was made by dissolving 25 gms. crystallized $CuSO_4$ in water, adding NH_4OH, and diluting to 1 litre. The decolorizing effect of KCy upon the ammoniacal solution of Cu is depended on to give the means for determining the amount of KCy present. The use to which it is proposed to apply the test is in determining the strength of KCy and its solutions for gold extractions.

Prussian Blue Determination. Coffingnier (*Bull. Soc. Chim.*, XXXI., 391). The method depends upon the solubility of Prussian blue in a mixture of equal parts HCl and propyl alcohol (or other alcohols of that series) from which it may be completely precipitated by dilution with water.

Treat 2 gms. of the pigment with 100 c.c. of the solvent—when all the blue has dissolved make up to 200. Filter from the insoluble portion, and treat 100 c.c. of the filtrate with water. Wash by decantation, collect on a weighed filter, dry and weigh. When much Al_2O_3 is present the blue dissolves with difficulty, but it is readily effected when $BaSO_4$, kaolin, etc., has been used. The larger the proportion of blue present, the less water required for complete precipitation.

Mercury Fulminate. Brownsdon (*Chem. News*, LXXXIX., 303). When the fulminate is decomposed by excess of $Na_2S_2O_3$ the resulting solution is alkaline, and the amount of fulminate present may be determined simply by titrating the solution with N/10 acid (H_2SO_4). The solution is best standardized by comparison test with results on pure fulminate. This is obtained by dissolving 1 mol. of the commercial salt in solution of KCy (1 mol.) precipitating with dilute HNO_3 washing free from acid and drying at 80° to 90°. 0.05 of the salt, or of the sample, is weighed out into a 100 c.c. flask containing 50 c.c. of water; 1 gm.

$Na_2S_2O_3$ crystals is added and the flask shaken until the fulminate has dissolved. Then dilute to 100 c.c., and after mixing, filter off portions of 25 c.c. each for titration.

Argon in the Atmosphere. Moissan (*Bull. Soc. Chim.*, XXXI., 729). About one litre of the air, after being dried by confining over metaphosphoric acid for several hours, was made to pass repeatedly for three hours through two tubes kept at red heat, until the manometer showed no further absorption (remaining at a constant level.) The first tube contained a mixture of CaO and Mg, the second about 1 gm. metallic Ca in small crystals. The residual gas was finally measured over mercury. In general terms the air over the land at different heights was found to contain 0.932 to 0.935 per cent. argon. Over the ocean, the proportion was slightly more.

Stability of Nitrocellulose. Bergmann and Junk (*Zts. Angew. Chem.*, XVII., 982 and 1074). The results of a research on this subject indicate that the best test consists in the determination of the amount of NO evolved from the sample by two hours heating at 132°C. A good nitrocellulose should not afford over 2.5 c.c. per gramme by this treatment. For collodion cottons, this limit may be reduced to about 2 c.c. The method will serve as a control in the process of manufacture. Presence of other substances as water, Na_2CO_3 $CaCO_3$ etc., affect the test insofar as they exert more or less influence toward hastening or retarding decomposition.

Washing nitrocellulose with alcohol improves its stability. Long heating at 132°C. increases its solubility in ether-alcohol.

Organic Matter in Water. Lenormand (*Bull. Soc. Chim.* [3], XXIX., 310, *ib.*, XXXI., No. 3). The method consists in the use of $K_2Mn_2O_8$ in alkaline solution, and determination of the excess by use of a colorimeter. Clarifying the water for the test by passing it through a filter paper was found to be a source of large error. Repeated washing of a filter with the same water showed a steady diminution in the amount of organic matter given up by the paper, but eight to ten lots of water hardly sufficed to clean the paper.

Calorimetric work — Forms of Sulphur in Coal. Somermeier (*J. Am. Chem. Soc.*, XXVI., 764).

S present as $FeSO_4$: loss of 10 cal. for each per cent. of sulphur.
" " " iron pyrites : gain of 9.6 cal. for each per cent. of sulphur.
" " " organic : loss of 4.5 cal. for each per cent. of sulphur.

When iron pyrites is present, if a correction is made for the O in the ash the calorimetric results are too low by 6.6 cal. for each per cent. of S present.

BOOK REVIEWS.

Notes on Assaying and Metallurgical Laboratory Experiments. By RICHARD W. LODGE. New York, John Wiley & Sons, 1904. 8vo, viii + 287 pages. $3.

Chapter I. consists of twenty-two pages, devoted to balances, weights, reagents, furnaces, fuels, crucibles, scorifiers, cupels, etc.

Chapter II. treats of sampling in fourteen pages, giving this most important operation the prominence it deserves.

Chapter III., seventy-four pages, is given up entirely to the assay of ores of silver. The plan of considering the assay of silver separately from that of gold is open to objection: in the first place, it is very seldom done in practice; in the second, it involves either repetition or cross references when the assay for gold is taken up. The first assay described in detail is that of copper matte, which does not seem desirable for a student at the beginning of his course. Many valuable tables are given showing the percentage of lead absorbed by the cupel, the losses of silver in cupellation at different temperatures, etc. The explanations of the effect of fluxes, especially the use of iron in crucible assays and the addition of silica in scorification, are excellent. The reducing power of ores is treated in much detail, many experiments made by students being given in full. A few awkward expressions or misprints are to be found as, page 106, "the lead buttons will weigh as recommended" and "Hydrate of copper, insoluble in excess of ammonia, etc."

Chapter IV., on the assay of ores for gold, fifty-seven pages, while excellent in most parts offers a few points for criticism: The statement that "an alloy containing less than 2½ parts of Ag to 1 part of Au will not part" contradicts the prevailing opinion. In parting, when the ratio of silver to gold is large, acid much weaker than that given, 1.13 sp. gr., is preferred by many. Under telluride ores, the scorification assay is still given, although it is condemned by the figures quoted and has been generally abandoned. The precautions in regard to fine grinding with rich telluride ores are important and universally acknowledged. Surcharge is defined as the amount of silver left in the gold after parting, while the usual meaning is given in a foot-note. This chapter, under special methods, contains a long article, 17 pages, on the assay of zinc-box residues, reprinted from the *Transactions of the American Institute of Mining Engineers*, which criticizes an article in the SCHOOL OF MINES QUARTERLY for January, 1901, by Fulton and Crawford. It is only necessary to point out here, that the materials contained very different percentages of zinc and in one case considerable copper and that the full discussion has appeared in the *Transactions*.

Chapter V., seven pages on the assay of ores for lead, is short but includes all that is essential. Adding iron to prevent loss of lead as silicate even when it is not required as a desulphurizing agent is given a well deserved prominence.

Chapter VI., fourteen pages, treats of the assay of bullion. The description of the determination of gold in gold bullion, while adequate, is

in no respect equal to that in Rose's Metallurgy of Gold. The time-honored and standard method of Gay-Lussac for silver in silver bullion is dismissed with a reference, while the Volhard method is described in detail.

Chapter VII., Asssay of ores for copper and tin, ten pages. Under copper, the Cornish method is given, as well as a method for Lake Superior ores. The best description of this method is in the *Journal of the American Chemical Society*, 24, 699. The treatment of the tin assay is brief and satisfactory, though finely ground anthracite is to be preferred to charcoal in the German method and Winkler's method deserves mention.

Chapter VIII., seventeen pages on platinum and the platinum group. This subject is treated in a somewhat different manner from those which precede, qualitative tests and tables of solubility being given, as well as directions for making assays. The prominence given to platinum is one of the best features of the book, as the interference of this group of metals is too often ignored by assayers.

Metallurgical Laboratory Experiments and Notes, sixty pages, describes the chlorination of gold ores, cyanide extraction tests, the melting and refining of bullion, retorting mercury and the chloridization of silver ores. Only a few of the purely chemical points are open to criticism.

The book as a whole is an important and valuable addition to the existing literature on assaying, very properly defined by the author as a branch of analytical chemistry. It will prove of great use to thoughtful assayers and is calculated to teach students to think about their work and to discard the rule of thumb methods which have too long prevailed. It is, however, badly arranged for a text book for beginners in the subject. Experiments by students are given in tiresome detail, often without any practicular conclusions being drawn from them; experiments which, while they show a most commendable desire to investigate, are in some cases mere repetitions, given without credit to those who have worked on similar lines.

While many omissions from the old works on assaying are desirable, corrected assays, the sampling of pig copper, the assay of cyanide solutions and other subjects of importance at the present time, are not adequately treated.

The length of this review is in itself proof that the work is considered of value. E. H. M.

NOVEMBER 30, 1904.

The Chemistry of Cyanide Solutions Resulting from the Treatment of Ores. By J. E. CLENNELL. New York and London, The Engineering and Mining Journal, 1904, 8vo, 164 pages. Price, $2.50.

The subject-matter is divided into eight classes, as follows: (1) The estimation of total cyanogen including all the methods with notes on their relative value, the estimation of hydrocyanic acid and of available cyanide. (2) Alkaline constituents, total alkali, protective alkali, hydrates, carbonates, ammonia. (3) Reducing agents, reducing power, ferrocyanides (many methods) thiocyanates, sulphides. (4) Auxiliary agents, oxygen, active kaloids, peroxides, ferricyanides. (5) Inactive bodies, cyanates and isocyanates chlorides, sulphates, etc. (6) Noble

metals, gold and silver together, including evaporation with litharge, evaporation in lead foil, precipitation by cuprous chloride, precipitation by cupric sulphate, etc. Gold alone, by reduction with zinc. Silver alone, precipitation as sulphide and cupellation, volumetric by sodium sulphide. (7) Base metals, zinc, by the ferrocyanide and sulphide methods, and copper. (8) Suspended matter.

Also the examination of various methods for the estimation of ferrocyanides including a critical comparison of many methods.

The book is a careful collection of the analytical methods which have been proposed and used in connection with cyanide solutions, made more valuable by the author's notes and comparisons. It should be in the hands of every chemist connected with a cyanide plant, for only by obtaining this book can he find the material which has appeared in the different chemical and mining journals without a lengthy search in some large library. E. H. M.

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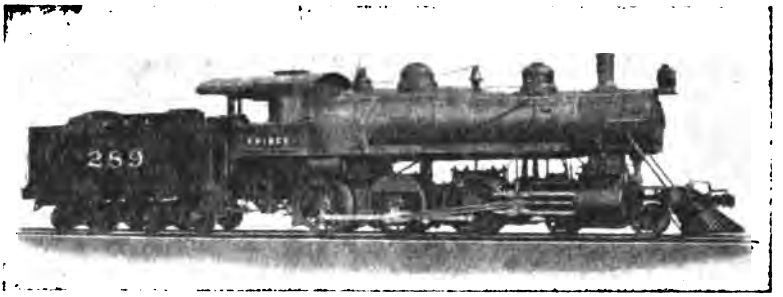

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VOL. XXVI. APRIL, 1905. No. 3.

NOTES ON ORGANIC ANALYSIS. PART III.

BY HENRY C. SHERMAN.

CHAPTER VII.

Carbohydrates—Special Methods.

(*Continued.*)

THE DETERMINATION OF STARCH.

METHOD OF DIRECT ACID HYDROLYSIS.

This method is accurate for the determination of starch in such samples as contain no other substance insoluble in water and capable of yielding reducing sugar on heating with dilute acid. It is now well known that such interfering substances, especially the pentosans, are generally found in vegetable tissues, and that the results obtained by direct acid hydrolysis are usually too high. This is, however, the method which has been commonly used until recently and for comparisons with earlier work determinations by direct hydrolysis are still frequently required.

*Conversion of Starch to Dextrose.**

Weigh 2 to 5 grams and, if much fat is present, wash with four or five successive portions each 10 c.c. of ether; allow the ether to evaporate, and wash with 150 c.c. of 10 per cent. alcohol to remove soluble carbohydrates. Wash the residue into a 250 c.c.

* Sachsse: *Chem. Centrbl.*, 1877, 732; Bul. 46, Bur. Chem. U. S. Dept. Agriculture.

flask with 200 c.c. of water, add 20 c.c. of hydrochloric acid of 1.125 sp. gr., and heat in a boiling water bath with a reflux condenser for two and one-half hours. Cool to room temperature, nearly neutralize with sodium hydroxide, dilute to 250 c.c.; filter, and determine dextrose in a portion of the filtrate, using either Defren's method, already described, or Allihn's method, as follows:

*Allihn's Method for the Determination of Dextrose.**

Reagents. — (1) 34.64 grams of crystallized copper sulphate dissolved in water and diluted to 500 c.c.

(2) 173 grams of sodium potassium tartrate and 125 grams of potassium hydroxide dissolved in water and diluted to 500 c.c.

Determination. — Place 30 c.c. of the copper solution, 30 c.c. of the alkaline tartrate solution and 60 c.c. of water in a beaker or casserole and heat to boiling. To the boiling liquid add 25 c.c. of the dextrose solution, note the time at which the mixture begins to boil and continue the boiling for exactly two minutes. Filter at once and obtain the weight of copper in the precipitated cuprous oxide by any of the methods suggested in connection with Defren's process described in Chapter V, or as follows: Collect the cuprous oxide on an asbestos filter in a Gooch crucible; wash the precipitate (including any which may adhere to the beaker and which need not be transferred to the filter) thoroughly with hot water, transfer the asbestos and adhering oxide from the crucible to the beaker. Dissolve the oxide still remaining in the crucible by means of 1 to 2 c.c. of concentrated nitric acid, adding the acid from a pipette and receiving the solution in the beaker containing the asbestos and the main part of the precipitate. Rinse the crucible with a jet of water allowing the rinsings to flow into the beaker. Heat the contents of the beaker until all copper is in solution; filter, wash thoroughly, dilute the filtrate to 100 to 150 c.c., add one drop of concentrated sulphuric acid and determine copper by electrolysis. Find the corresponding weight of dextrose from Allihn's table.

Notes. — The conditions described must be observed carefully. The dextrose solution added to the copper reagent must be free from turbidity and only faintly acid. The rapid addition of this cold solution stops the boiling of the reagent, and it is well to have the heat so regulated that the mixture will boil again in about

* *Journ. prakt. Chem.*, 1880, **22**, 46; Bul. 46, *loc. cit.*

ALLIHN'S TABLE FOR THE DETERMINATION OF DEXTROSE.

Milligrams of Copper.	Milligrams of Dextrose.	Milligrams of Copper.	Milligrams of Dextrose.	Milligrams of Copper.	Milligrams of Dextrose.	Milligrams of Copper.	Milligrams of Dextrose.	Milligrams of Copper.	Milligrams of Dextrose.
10	6.1	67	34.3	124	63.1	181	92.6	238	122.8
11	6.6	68	34.8	125	63.7	182	93.1	239	123.4
12	7.1	69	35.3	126	64.2	183	93.7	240	123.9
13	7.6	70	35.8	127	64.7	184	94.2	241	124.4
14	8.1	71	36.3	128	65.2	185	94.7	242	125.0
15	8.6	72	36.8	129	65.7	186	95.2	243	125.5
16	9.0	73	37.3	130	66.2	187	95.7	244	126.0
17	9.5	74	37.8	131	66.7	188	96.3	245	126.6
18	10.0	75	38.3	132	67.2	189	96.8	246	127.1
19	10.5	76	38.8	133	67.7	190	97.3	247	127.6
20	11.0	77	39.3	134	68.2	191	97.8	248	128.1
21	11.5	78	39.8	135	68 8	192	98.4	249	128.7
22	12.0	79	40.3	136	69.3	193	98.9	250	129.2
23	12.5	80	40.8	137	69.8	194	99.4	251	129.7
24	13.0	81	41.3	138	70.3	195	100.0	252	130.3
25	13.5	82	41.8	139	70.8	196	100.5	253	130.8
26	14.0	83	42.3	140	71.3	197	101.0	254	131.4
27	14.5	84	42.8	141	71.8	198	101.5	255	131.9
28	15.0	85	43.4	142	72.3	199	102.0	256	132.4
29	15.5	86	43.9	143	72.9	200	102.6	257	133.0
30	16.0	87	44.4	144	73.4	201	103.1	258	133.5
31	16.5	88	44.9	145	73.9	202	103.7	259	134.1
32	17.0	89	45.4	146	74.4	203	104.2	260	134.6
33	17.5	90	45.9	147	74.9	204	104.7	261	135.1
34	18.0	91	46.4	148	75.5	205	105.3	262	135.7
35	18.5	92	46.9	149	76.0	206	105.8	263	136.2
36	18.9	93	47.4	150	76.5	207	106.3	264	136.8
37	19.4	94	47.9	151	77.0	208	106.8	265	137.3
38	19.9	95	48.4	152	77.5	209	107.4	266	137.8
39	20.4	96	48.9	153	78.1	210	107.9	267	138.4
40	20.9	97	49.4	154	78.6	211	108.4	268	138.9
41	21.4	98	49.9	155	79.1	212	109.0	269	139.5
42	21.9	99	50.4	156	79.6	213	109.5	270	140.0
43	22.4	100	50.9	157	80.1	214	110.0	271	140.6
44	22.9	101	51.4	158	80.7	215	110.6	272	141.1
45	23.4	102	51.9	159	81.2	216	111.1	273	141.7
46	23.9	103	52.4	160	81.7	217	111.6	274	142.2
47	24.4	104	52.9	161	82.2	218	112.1	275	142.8
48	24.9	105	53.5	162	82.7	219	112.7	276	143.3
49	25.4	106	54.0	163	83.3	220	113.2	277	143.9
50	25.9	107	54.5	164	83.8	221	113.7	278	144.4
51	26.4	108	55.0	165	84.3	222	114.3	279	145.0
52	26.9	109	55.5	166	84.8	223	114.8	280	145.5
53	27.4	110	56.0	167	85.3	224	115.3	281	146.1
54	27.9	111	56.5	168	85.9	225	115.9	282	146.6
55	28.4	112	57.0	169	86.4	226	116.4	283	147.2
56	28.8	113	57.5	170	86.9	227	116.9	284	147.7
57	29.3	114	58.0	171	87.4	228	117.4	285	148.3
58	29.8	115	58.6	172	87.9	229	118.0	286	148.8
59	30.3	116	59.1	173	88.5	230	118.5	287	149.4
60	30.8	117	59.6	174	89.0	231	119.0	288	149.9
61	31.3	118	60.1	175	89.5	232	119.6	299	150.5
62	31.8	119	60.6	176	90.0	233	120.1	290	151.0
63	32.3	120	61.1	177	90.5	234	120.7	291	151.6
64	32.8	121	61.6	178	91.1	235	121.2	292	152.1
65	33.3	122	62.1	179	91.6	236	121.7	293	152.7
66	33.8	123	62.6	180	92.1	237	122.3	294	153.2

ALLIHN'S TABLE FOR THE DETERMINATION OF DEXTROSE.—*Continued.*

Milligrams of Copper.	Milligrams of Dextrose.	Milligrams of Copper.	Milligrams of Dextrose.	Milligrams of Copper.	Milligrams of Dextrose.	Milligrams of Copper.	Milligrams of Dextrose.	Milligrams of Copper.	Milligrams of Dextrose.
295	153.8	329	172.5	363	191.7	397	211.2	431	231.0
296	154.3	330	173.1	364	192.3	398	211.7	432	231.6
297	154.9	331	173.7	365	192.9	399	212.3	433	232.2
298	155.4	332	174.2	366	193.4	400	212.9	434	232.8
299	156.0	333	174.8	367	194.0	401	213.5	435	233.4
300	156.5	334	175.3	368	194.6	402	214.1	436	233.9
301	157.1	335	175.9	369	195.1	403	214.6	437	234 5
302	157.6	336	176.5	370	195.7	404	215.2	438	235.1
303	158.2	337	177.0	371	196.3	405	215.8	439	235.7
304	158.7	338	177.6	372	196.8	406	216.4	440	236.3
305	159.3	339	178.1	373	197.4	407	217.0	441	236.9
306	159.8	340	178.7	374	198.0	408	217.5	442	237.5
307	160.4	341	179.3	375	198.6	409	218.1	443	238.1
308	160.9	342	179.8	376	199.1	410	218.7	444	238.7
309	161.5	343	180.4	377	199.7	411	219.3	445	239.3
310	162.0	344	180.9	378	200.3	412	219.9	446	239.8
311	162.6	345	181.5	379	200.8	413	220.4	447	240.4
312	163.1	346	182.1	380	201.4	414	221.0	448	241.0
313	163.7	347	182.6	381	202.0	415	221.6	449	241.6
314	164.2	348	183.2	382	202.5	416	222.2	450	242.2
315	164.8	349	183.7	383	203.1	417	222.8	451	242.8
316	165.3	350	184.3	384	203.7	418	223.3	452	243.4
317	165.9	351	184.9	385	204.3	419	223.9	453	244.0
318	166.4	352	185.4	386	204.8	420	224.5	454	244.6
319	167.0	353	186.0	387	205.4	421	225.1	455	245.2
320	167.5	354	186.6	388	206.0	422	225.7	456	245.7
321	168.1	355	187.2	389	206.5	423	226.3	457	246.3
322	168.6	356	187.7	390	207.1	424	226.9	458	246.9
323	169.2	357	188.3	391	207.7	425	227.5	459	247.5
324	169.7	358	188.9	392	208.3	426	228.0	460	248.1
325	170.3	359	189.4	393	208.8	427	228.6	461	248.7
326	170.9	360	190.0	394	209.4	428	229.2	462	249.3
327	171.4	361	190.6	395	210.0	429	229.8	463	249.9
328	172.0	362	191.1	396	210.6	430	230.4		

two minutes, then after exactly two minutes of actual boiling remove the flame and filter the solution at once. The cuprous oxide is very apt to run through the filter. To prevent this, after making the asbestos filter as usual, pour on it some very fine asbestos suspended in water, so as to form a tight layer on the top of the felt. On the assumption that the starch is quantitatively hydrolyzed to dextrose, the weight of the latter multiplied by 0.9 gives the corresponding weight of starch. For detailed studies of the hydrolysis of starch by acids, see the papers of Rolfe* and of Noyes.†

* *Journ. Amer. Chem. Soc.*, 1896, 18, 869; 1897, 19, 261; 1903, 25, 1003, 1015.

† *Ibid.*, 1904, 26, 266.

According to several investigators,* the weight of dextrose should be multiplied by a higher factor (0.917 to 0.941) rather than 0.9, to find the corresponding weight of starch.

Method of Digestion with Diastase or Saliva.

If starch is gelatinized by boiling with water and then treated with malt diastase or saliva, it can be converted into maltose and dextrin and these separated by filtration from the insoluble residue containing the pentosans and other substances which cause the results by the preceding method to be too high.

Determination. — Extract 2.5 to 5 grams of sample with five successive portions each 10 c.c. of ether, decanting the washings through a hardened filter; wash with 150 c.c. of 10 per cent. alcohol;† transfer the residue to a beaker with 50 to 100 c.c. of water; heat gradually to boiling, stirring constantly to prevent bumping or the formation of lumps. Cool to 55° for diastase, or to 38° for saliva; add the solution containing the enzyme and keep the mixture within two degrees of the stated temperature until a drop, removed and tested on a porcelain plate, no longer shows a reaction for starch on mixing with a drop of dilute solution of iodine in aqueous potassium iodide. Now heat the solution again to boiling in order to gelatinize any starch granules which may remain; test the solution, and if starch is found, cool to the proper temperature; add more of the enzyme and digest as before. Continue this treatment until the solution gives no starch reaction after boiling, or until a careful microscopic examination shows that the insoluble residue is entirely free from starch. Dilute to 250 c.c., mix thoroughly and pour on a dry fluted filter. Transfer 150 c.c. of the filtrate to a 250 c.c. flask; add 15 c.c. of hydrochloric acid of 1.125 sp. gr., attach the flask to a reflux condenser and heat in a boiling water-bath for two and one-half hours, or boil gently on a hot plate or sand-bath for 35 to 45 minutes. Complete the determination as described in the preceding method.

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* Salomon: *Ztschr. anal. Chem.*, 1883, 22, 593. Soxhlet: *Wochenschr. für Brauer.*, 1885, 193; Vaubel, II., 455. Sostegni: *Chem. Centrbl.*, 1887, 58, 896. Lintner and Düll: *Ztschr. angew. Chem.*, 1891, 537. Ost: *Chem. Ztg.*, 1895, 19, 1502. Rössing: *Ztschr. öffentl. Chem.*, 1904, 10, 61; Abs. *Journ. Chem. Soc.*, 1904, 86, ii, 298. Noyes: *Journ. Amer. Chem. Soc.*, 1904, 26, 280.

† This extraction can often be omitted, since for many purposes it is unnecessary to distinguish between starch and soluble carbohydrates.

The determination should be carried through without interruption. If this is impossible, care must be taken to avoid alcoholic or lactic fermentation. After the digestion with the enzyme is finished, but not before, salicylic acid may be added as a preservative. It has been recommended that a trace of fluoride be added at the start to retard lactic fermentation while the digestion with the enzyme is taking place.

When only a few determinations are to be made, freshly collected saliva can conveniently be used, as this is free from carbohydrate. If commercial diastase or an infusion of malt * is used, the amount added must be noted and a correction applied for the carbohydrate thus introduced. This is found by heating a quantity of the diastate or infusion with acid and determining the resulting dextrose as in the starch determination.

Comparison of Results.

The diastase method, carefully carried out, is believed to yield practically correct results. As already explained, the results obtained by direct acid hydrolysis are usually higher owing to the presence of other substances which yield reducing sugars. A comparison of the results of the two methods is of considerable interest, both because many of the recorded determinations

Results by Diastase and by Direct Acid Hydrolysis.

Substance.	Starch Indicated by		Substance.	Starch Indicated by	
	Diastase Method Per Cent.	Acid Method. Per Cent.		Diastase Method Per Cent.	Acid Method Pe Cent.
Air-dry starch.....	82.49	82.30	White pepper†.....	56.47	59.17
Wheat flour.....	66.55	68.35	Long pepper†.....	39.55	42.88
Oatmeal.....	56.23	59.01	Black pepper†..	34.15	38.63
Graham flour.....	55.32	58.63	Mace †.....	27.87	31.73
Wheat bran.....	20.97	38.82	Nutmeg †.....	23.72	25.56
Linseed meal†.....	14.06	21.15	Allspice†.....	3.04	18.03
Cocoa nibs†.....	8.07	11.16	Cloves †.....	2.74	8.99
Wheat straw.....	4.39	22.69	Pepper shells†.....	2.30	11.43
Cocoa shells†.....	4.14	18.03	Cayenne†.....	1.01	8.47
Buckwheat hulls†....	1.46	20.51	Walnut shells†.....	1.01	19.30
Corn stover.....	0.96	20.13	Almond shells†.....	0.84	22.72

* An active malt infusion can be prepared by digesting 10 grams of fresh, finely-ground malt, over night at room temperature, with 200 c.c. of water or 10 per cent alcohol.

† Results by Winton and associates, compiled from Leach's Food Inspection and Analysis.

of starch were made by the acid method and because the determination of copper-reducing substance obtained by direct hydrolysis is sometimes used as a means of detecting adulterants in spices. The table below shows the results of comparison of the two methods on a variety of substances. Many of the results of Winton and associates are averaged from the comparative examination of several samples. The other results were obtained by the writer, only one sample of each kind being examined.

Determination of Starch in Meat Products.

Starchy materials are sometimes added as "fillers" to sausages and other forms of chopped meat. This adulteration is easily detected by the iodine reaction which, however, must be carefully interpreted since a small amount of starch may legitimately be present from the spices added in the manufacture. The quantitative determination is complicated by the fact that meat appears to contain some substance which interferes with the separation of the cuprous oxide reduced in applying the usual method. Advantage is therefore taken of the insolubility of starch in alcoholic, and its solubility in aqueous potassium hydroxide. The method of Mayrhofer as modified by Bigelow and adopted by the Association of Official Agricultural Chemists is as follows:*

Treat from 10 to 20 grams of the sample under examination (depending upon the amount of starch indicated by the iodine reaction) in a porcelain dish or casserole with 50 c.c. of an 8 per cent. solution of potassium hydroxide and heat the mixture on the water-bath until the meat is entirely dissolved. Add an equal volume of 95 per cent. alcohol, mix thoroughly, filter the mixture through an asbestos filter and wash twice with a hot 4 per cent. solution of potassium hydroxide in 50 per cent. alcohol. Then wash with 50 per cent. alcohol until a small portion of the filtrate does not become turbid upon the addition of acid. Return the precipitate and filter to the original vessel and dissolve the precipitate with the aid of heat in 60 c.c. of a normal solution of potassium hydroxide. In the case of sausage with a high starch content a somewhat larger volume of alkali may be required. Acidify the filtrate strongly with acetic acid, dilute to a definite volume, mix thoroughly by shaking, filter through a fluted paper, and precipitate the starch from an aliquot part of the filtrate by means of

* Bul. 65, Bur. Chem., U. S. Dept. Agriculture.

an equal volume of 95 per cent. alcohol. Transfer the precipitate to a weighed filter, wash thoroughly with 50 per cent. alcohol, with absolute alcohol, and finally with ether, dry to a constant weight at the temperature of boiling water and weigh.

Additional References.

Wiley: Agricultural Analysis, Vol. III.
Winton: *Journ. Anal. Appl. Chem.*, 1888, **2**, 153.
Hibbard: *Journ. Amer. Chem. Soc.*, 1895, **17**, 64.
Ost: *Chem. Ztg.*, 1895, **19**, 1501.
Stone: *Journ. Amer. Chem. Soc.*, 1894, **16**, 726.
Sherman: *Analyst*, 1897, **22**, 19.
Wiley and Krug: *Journ. Amer. Chem. Soc*, 1898, **20**, 253, 266.
Lintner: *Ztschr. angew. Chem.*, 1898, 725.
Lindet: *Journ. Pharm. Chim.*, 1901, [6], **14**, 397.
Witte: *Ztschr. Unters. Nahr.-Genussm.*, 1904, **7**, 65.

SEPARATION OF CARBOHYDRATES IN CEREAL PRODUCTS.

Determination of Reducing Sugars, Sucrose, Dextrin, Starch, Pentosans and Cellulose.

The following scheme * provides for each of the substances or groups mentioned and avoids the danger (inherent in the usual plan of making a number of independent determinations) of including the same substance as a constituent of more than one group.

Free the sample from fat by washing with ether.

Extract with boiling alcohol.

Solution A.— Evaporate the alcohol, dilute with water and determine the reducing power of portions of the solution before and after hydrolysis. Calculate the *reducing sugar* and *sucrose*.

Residue A.— Extract with cold water.

Solution B. — Hydrolyze a portion and determine the resulting dextrose, calculate *dextrin* and *soluble starch*. In another portion, precipitate soluble starch by barium hydroxide,† filter and determine *dextrin* in the filtrate.

Residue B. — Boil with water and treat with malt extract or saliva, filter and wash thoroughly.

* Based on the following papers: Stone; *Journ. Amer. Chem. Soc.*, 1897, **19**, 183. Sherman; *Ibid.*, 1897, **19**, 291. Browne and Beistle; *Ibid.*, 1901, **23**, 229.

† Asboth: *Chem. Ztg.*, 1889, **13**, 591.

Solution C. — Hydrolyze, determine resulting dextrose and calculate *starch.*

Residue C. — Boil with 2 per cent. hydrochloric or sulphuric acid until the maximum reducing power of the solution is reached.*

Solution D. — Determine reducing power in the same manner as for dextrose. Calculate as xylose, the reducing power of which is 1.03 times that of dextrose. † From the pentose thus found calculate the percentage of *pentosan.* In the case of wheat it has been found ‡ that the material ("hemicellulose") dissolved and hydrolyzed at this point is entirely pentosan. The same is probably true of the other cereals. The pentosan thus dissolved and hydrolyzed does not include necessarily the entire furfurol-yielding substance of the cereal.

Residue D. — Boil for 30 minutes with 1 per cent. sodium hydroxide, filter and wash, press out most of the water and expose the moist fiber to chlorine gas for one hour. Wash with water, boil with a solution containing 2 per cent. sodium sulphite and 0.2 per cent. sodium hydroxide; filter, wash with warm water until the washings are neutral and colorless, then wash with strong alcohol, dry and weigh. Deduct the ash which the residue contains and calculate the organic matter as *cellulose.* §

Determination of Maltose, Dextrin and Starch in Malted Cereal.

The absence of any considerable amount of dextrose or invert-sugar must be shown by stirring some of the sample with about ten times its weight of water and testing the filtered extract by means of phenylhydrazine or Barfoed's solution as described in Chapter V. If no monosaccharide is present the percentages of maltose, dextrin and starch can be estimated as follows:

Mix 5 grams of sample with 125 c.c. of cold water‖ in a 250 c.c.

* For sulphuric acid this was found to be 4 to 6 hours. Stone prefers hydrochloric acid and states that the reaction is nearly complete in 1 hour.

† Stone: *Amer. Chem. Journ.*, 1891, 13, 82. Since the reducing power of arabinose does not differ greatly from that of xylose, this calculation would still be nearly correct in case both pentoses were present.

‡ *Journ. Amer. Chem. Soc.*, 1897, 19, 294.

§ This is the method of Cross and Bevan. For a comparison of this with other methods see *Journ. Amer. Chem. Soc.*, 1897, 19, 304.

‖ If the sample contains an active enzyme some of the carbohydrate may be changed during this treatment with water. To prevent this a very dilute alkali solution, containing 0.02 per cent. potassium hydroxide or an equivalent amount of sodium or ammonium hydroxide, may be used. Ling and Rendle: *Journ. Inst. Brewing*, 1904, 10, 238; Abs. *Journ. Chem. Soc.*, 1904, 86, ii., 507.

flask; allow to stand at room temperature for one hour, shaking frequently; fill to the mark, shake and filter through dry paper. Determine reducing power of one or more 25 c.c. portions of this filtrate by either Defren's or Allihn's method and calculate the amount of maltose.* Measure 50 c.c. of the same filtrate into a 100 c.c. flask, add 5 c.c. of hydrochloric acid of 1.125 sp. gr. and hydrolyze as in the determination of starch. Determine the resulting dextrose, deduct the amount due to maltose and estimate the remainder as due to dextrin. Soluble starch if present would be counted as dextrin in this analysis.

Treat another portion of the original sample as described under the determination of starch, but without extracting the soluble carbohydrates. From the dextrose found, subtract that yielded by maltose and dextrin and estimate the remainder as derived from starch.

The results require a slight correction on account of the presence of the insoluble residue when the solution is diluted to volume in the graduated flask. Although some details of the method are open to criticism, it gives results sufficiently exact for the purpose for which it is mainly used, which is to show whether the starch of the cereal has been largely changed to soluble products.

The same plan may be used in the examination of cereal foods prepared by parching or in other ways, provided only one reducing sugar is present in appreciable quantity. The amount of soluble carbohydrate in such preparations is usually too small for satisfactory determination by means of the polariscope.

REFERENCES TO OTHER SPECIAL METHODS.

Substances Rich in Sucrose or Invert-sugar.

Detection of Sucrose.

Wiley: Agricultural Analysis, Volume III., 189. Leach: Food Inspection and Analysis, 480.

Determination of Sucrose, Dextrose and Levulose.

Wiechmann: *Journ. Anal. Appl. Chem.*, 1890, **4**, 253; 1891, **5**, 401; *Ztschr. anal. Chem.*, 1891, **30**, 78. Wiley: *l. c.*, 280–286, 307–308. Vaubel: Bestimmung organischer Verbindungen, Band II., 447–450.

* If Allihn's method is used, assume the reducing power of maltose to be 0.61 that of dextrose.

Direct Determination of Levulose.

Allen: Commercial Organic Analysis, Vol. I. (3d Ed.) 356.
Wiley: *l. c.*, 267–274; *Journ. Amer. Chem. Soc.*, 1896, **18**, 81.

Determination of Sucrose and Commercial Glucose.

Chandler and Ricketts: Tucker's Manual of Sugar Analysis, 287.
Weber and McPherson: *Journ. Amer. Chem. Soc.*, 1895, **17**, 312.
Mathews and Parker: *Analyst*, 1900, **25**, 89.
Leach: *l. c.*, 504–513; *Journ. Amer. Chem. Soc.*, 1903, **25**, 982.
Gudeman: U. S. Dept. Agriculture, Bur. Chem., Bul. 73, p. 65.

Determination of Sucrose and Raffinose.

Lippmann: Chemie der Zuckerarten, Band II., 1654–1661.
Davoll: *Journ. Amer. Chem. Soc.*, 1903, **25**, 1019.
Bul. 46, Bur. Chem., U. S. Dept. Agriculture.

Determination of Moisture.

Wiley: Agricultural Analysis, Volume III., 13–36.

Interpretation of Results.

Molasses and Syrup. — Bul. 13, Part 6, Div. Chem., U. S. Dept. Agriculture.
Bodman, Leonard and Smith: *Analyst*, 1899, **24**, 253.
Jones: *Ibid.*, 1900, **25**, 87.
Miller and Potts: *Journ. Soc. Chem. Ind.*, 1899, **18**, 1091.
Leonard: *Analyst*, 1900, **25**, 85.
Maple Products. — Leach, *l. c.*, 463, 767.
Hortvet: *Journ. Amer. Chem. Soc.*, 1904, **26**, 1523.
Honey. — Bul. 13, Part 6, *l. c.* Leach: *l. c.*, 511–514.
Bujard and Baier: Hilfbuch für Nahrungsmittel Chemiker, 208.
Beckmann: *Ztschr. anal. Chem.*, 1896, **35**, 263.
Hoitsema: *Ibid.*, 1899, **38**, 439.
Circular No. 13, Office of the Secretary, U. S. Dept. Agriculture.
Confectionery. — Leach: *l. c.*, 518–521, 630.
Bul. 65, Bur. Chem., U. S. Dept. Agriculture.

ARTIFICIAL MIXTURES CONTAINING LACTOSE.

Qualitative Examination.

Bartley and Mayer: Merck's Report 1903, **12**, 100. Leach, *l. c.*, 507. See also methods given in Chapter V.

Determination of Sucrose and Lactose.

In milk chocolate. — Laxa: *Ztschr. Unters. Nahr.-Genussm*, 1904, 7, 471.

In condensed milk. — Wiley: *l. c.*, 296–298.

Hyde: *Journ. Amer. Chem. Soc.*, 1899, 21, 439.

Riiber and Riiber: *Ztschr. anal. Chem.*, 1901, 40, 97.

Harrison: *Analyst*, 1904, 29, 248.

Determination of Sucrose, Lactose and Invert-sugar.

Bigelow and McElroy: *Journ. Amer. Chem. Soc.*, 1893, 15, 668.

Determination of Lactose and Maltose.

Boyden: *Journ. Amer. Chem. Soc.*, 1902, 24, 993. See also mucic acid method for lactose, Chapter V.

ANIMAL TISSUES AND FLUIDS OTHER THAN MILK.

Determination of Glycogen.

Pfluger: *Arch. ges. Physiol.*, 1899, 75, 120; 76, 531; 1904, 103, 169; Abs. *Journ. Chem. Soc.*, 1904, 86, ii, 595.

Salkowski: *Biochem. Centrbl.*, 1903, 1, 337.

Lebbin: *Pharm. Ztg.*, 1898, 43, 519; Abs. *Chem. Centrbl.*, 1888, II., 513.

Huppert: *Ztschr. physiol. Chem.*, 18, 137, 144.

Haywood: *Journ. Amer. Chem. Soc.*, 1900, 22, 85.

U. S. Dept. Agriculture, Bur. Chem., Bul. 65, p. 13.

Detection and Determination of Dextrose.

Hoppe-Seyler: Physiologisch- and Pathologisch-Chemische Analyse (Revised by Thierfelder, 1903), 88–96.

Vaubel: Bestimmung organischer Verbindungen, I., 183, 501–503; II., 307, 507–509.

Allen: *l. c.*, Volume I., 344–351.

Sutton: Volumetric Analysis (9th ed.), 321, 409.

Harley: *Journ. Physiol.*, 1891, 12, 391.

Long: *Journ. Amer. Chem. Soc.*, 1900, 22, 309, 592.

Raimann: *Ztschr. anal. Chem*, 1901, 40, 390.

CHAPTER VIII.

Acids.

Free organic acids when dissolved in water are dissociated to a small extent and can usually be determined by direct titration, using as standard alkali a solution of a strong base and as indicator a substance of very weak acid properties such as phenolphthalein. In cases where direct titration is not available, the determination of acidity can be made by an indirect method, such as allowing the substance to act upon a carbonate and collecting the carbon dioxide set free, or upon potassium iodate in the presence of an excess of iodide when each carboxyl hydrogen entering into reaction results in the liberation of one atom of iodine. The iodine thus liberated is determined by titration with standard thiosulphate. These and other methods for the determination of the carboxyl group are fully discussed by Meyer and Tingle.* Alkaline salts of organic acids are usually converted into carbonates by ignition, so that the determination of carbonate in the ash of a neutral or neutralized mixture often indicates the amount of organic acid present as salt before ignition.

ACETIC ACID AND ACETATES.

Pure acetic acid is a colorless liquid of 1.056 specific gravity, miscible in all proportions with water, alcohol, and ether. When nearly anhydrous it solidifies at about 16° — hence the term "glacial" as applied to very strong acetic acid. The pure acid boils without decomposition at 119°. From dilute aqueous solutions it distils readily with steam at the temperature of boiling water. The principal source of commercial acetic acid is the crude acetate of lime made by neutralizing the acid obtained in the dry distillation of wood. For the determination of the volatile acid obtainable from commercial acetate the following method can be used.

DETERMINATION OF ACETIC ACID IN CALCIUM ACETATE.

Arrange a round-bottomed flask of 300 c.c. capacity in such a way that it can be inclined at an angle of about 60° from the per-

* Determination of Radicles in Carbon Compounds.

pendicular and connected with a nearly vertical condenser, while another tube passing through the stopper of the flask provides for the continuous introduction of water, drop by drop, during the distillation. The flow of water can be controlled by means of a screw pinchcock or a small dropping funnel.

Weigh 2 grams of the ground sample,* transfer to the flask and add 15 c.c. of 50 per cent. phosphoric acid and 25 c.c. of water, being sure that the water washes down any of the sample or acid which may have adhered to the neck of the flask. Connect the flask with the condenser and distil, collecting the distillate in a receiver containing 50 c.c. of water to prevent loss due to evaporation of acetic acid. During the distillation keep the volume of liquid nearly constant at 40 c.c. by admitting water free from carbon dioxide, in such a way that the drops fall upon the inner surface of the neck of the flask and not directly into the boiling liquid. Continue the distillation until the distillate is no longer acid. This usually requires about one and one-half hours. Titrate the distillate with freshly standardized sodium hydroxide solution using phenolphthalein as indicator. Calculate the total acidity as percentage of acetic acid in the sample.

Notes. — It has been found that small amounts of phosphoric acid are frequently carried over mechanically if the acetic acid is removed by a current of steam or if the distillation is conducted in an upright flask, especially when drops of water are allowed to fall directly into the boiling acid mixture. The directions for arrangement of apparatus are intended to avoid this source of error.

The phosphoric acid used must not contain nitric or any other volatile acid. The large excess recommended dissolves the calcium phosphate formed and thus prevents bumping. Oxalic may be substituted for phosphoric acid, and the calcium oxalate removed by filtration before distilling. This method, however, is longer and no more accurate than the phosphoric acid method as described. Sulphuric acid cannot be used, as it would be partially reduced to sulphurous acid by the tarry matter present in the crude acetate.

The distillate obtained as described should contain only a minute amount of carbonic acid. It is frequently recommended that the distillate be caught in standard alkali nearly sufficient to neutralize

* In sampling, grinding, and weighing portions for analysis, special care must be taken to avoid changes in moisture content.

all the volatile acid expected. In this case the distillate would contain all carbonic acid liberated in the distillation. The distillate containing some free acetic acid should therefore be boiled under a reflux condenser to expel carbonic acid before making the final titration. Errors may also be caused by variation in the amount of carbonate in the alkali used for titration. Hence this must be freshly standardized, using phenolphthalein as indicator, under the same conditions of temperature and removal of carbon dioxide as exist in the titration of the distillate.

The volatile organic acid, though calculated as acetic, always contains some formic, propionic, and butyric acids. In addition to these Scheuer found small amounts of valerianic, caproic, heptylic, caprylic, and nonylic acids. In view of the danger of phosphoric acid being carried over, it is advisable, after titrating the distillate, to add nitric acid, evaporate to 25 c.c. and test for phosphoric acid by adding ammonium nitrate and molybdate solution.

The distillation method has now almost entirely replaced the indirect methods formerly used. There is, however, no general agreement as to the details of manipulation. A full description of the method as used in the laboratory of the General Chemical Company is given by Grosvenor.

References.

Allen: Commercial Organic Analysis, Volume I.

Sutton: Volumetric Analysis.

Scheuer: Analyse von Graukalk. Dissertation, Munich, 1902.

Stillwell: Acetic Acid in Acetate of Lime. *Journ. Soc. Chem. Ind.*, 1904, 23, 305.

Grosvenor: Analysis of Commercial Acetate of Lime. *Ibid.*, 1904, 23, 530.

SEPARATION OF ACETIC ACID FROM ITS HOMOLOGUES.

It was explained, in connection with the determination of alcohols, that methyl alcohol is oxidized to carbon dioxide and water by heating with sulphuric acid and potassium dichromate while ethyl alcohol is oxidized only to acetic acid. In the same way formic acid can be determined by oxidation with the dichromate mixture, acetic acid, if present, being unaffected by the treatment. The methods of Macnair * and Freyer † are based on this principle.

* *Chem. News*, 1887, 55, 229.

† *Chem. Ztg.*, 1895, 19, 1184.

According to Leys,* formic acid is also quantitatively oxidized by mercuric acetate. The reaction takes place readily on heating, even in very dilute solution, and is said to yield accurate results which are not affected by the presence of acetic acid, alcohol, or aldehyde.

Aside from the determination of formic acid by oxidation, the analysis of a mixture of closely related homologues is very difficult. Haberland proposed† a method for the separation of formic, acetic, propionic, and butyric acids in crude wood vinegar. This method involved the precipitation of propionic acid as basic lead propionate insoluble in water, and of formic acid as zinc formate insoluble in alcohol, after which the acetic and butyric acids were separated either by the difference in the solubilities of the silver salts or by fractional distillation of the amyl esters. According to Schütz,‡ however, these separations are far from quantitative.

Wechsler§ separated these acids qualitatively by the method of partial distillation, in which the mixture of acids is treated with an amount of alkali insufficient for complete neutralization, and then distilled. Under these conditions the higher homologues, although less volatile, are concentrated in the distillate, the lower and stronger acids remaining in combination with the base. Scheuer|| applied the same method quantitatively with good results but found it too long for practical purposes.

VINEGAR.

A thorough examination of vinegar should include determinations of specific gravity, total solids or extract, total and soluble ash, alkalinity and phosphoric acid of the ash, total and volatile acidity, and alcohol. Free mineral acids and oxalic acid should be determined if present and tests should be made for preservatives, poisonous metals, foreign pungent materials, and foreign colors.

Methods for all of these determinations have been adopted by the Association of Official Agricultural Chemists. The following directions for the more important determinations are in accordance with the official methods.

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* *Bull. Soc. Chim.*, 1898 [3], 19, 472; *Chem. News*, 1898, 78, 245. See also Sparre: *Ztschr. anal. Chem.*, 1900, 39, 105.

† *Ztschr. anal. Chem.*, 1899, 38, 217.

‡ *Ztschr. anal. Chem.*, 1900, 39, 17.

§ *Monatsh. Chem.*, 1893, 14, 462.

|| Ueber die Trennung und Bestimmung flüchtiger Fettsauren. Dissertation, Munich, 1902.

Solids and Ash.

Total Solids or Extract.

Evaporate 10 c.c. nearly to dryness in a weighed platinum dish of 50 mm. diameter on a steam bath, dry for two and one-half hours in a boiling water oven, cool thoroughly in a desiccator and then weigh quickly.

Total Ash.

Char the extract thoroughly at a low red heat, leach with water, burn the insoluble residue to whiteness, add the water solution, evaporate and heat to low redness, cool in a desiccator and weigh.

*Solubility and Alkalinity of Ash.**

Evaporate 25 c.c. to dryness, burn, cool and weigh; extract the ash repeatedly on an ash-free filter; dry and ignite the filter and residue, and weigh as insoluble ash. Titrate the filtrate using methyl orange as indicator, and calculate the number of c.c. of tenth-normal acid which would be required to neutralize the corresponding filtrate from 100 c.c. of the vinegar.

Total and Volatile Acids.

Total Acidity.

Dilute 10 c.c. in a beaker until the solution appears very light-colored against a white background, add phenolphthalein and titrate with standard sodium hydroxide. If only the total acidity is determined the result is expressed as acetic acid.

Volatile Acids.

Heat 15 c.c. of the vinegar to boiling in a flask, adding a little tannin to check foaming, if necessary; lower the flame and distil with steam until the distillate no longer contains acid. Titrate the distillate with standard sodium hydroxide and calculate as acetic acid.

The difference between the total acidity and that due to volatile acids gives a measure of the fixed acids and, in the case of cider vinegar, is calculated as malic acid.

* Smith's method modified by Frear: *Journ. Amer. Chem. Soc.*, 1898, 20, 5; Bul. 65, Bur. Chem., U. S. Dept. Agriculture.

Free Mineral Acids.

Detection by Methyl-Violet.

Dilute 5 c.c. of the vinegar with 5 to 10 c.c. water to reduce the acidity to about 2 per cent. of acetic acid, add four or five drops of an aqueous solution of methyl violet (one part of "methyl violet 2B" — No. 56 of Bayer Farbenfabrik, Elberfeld — in 10,000 parts of water). Mineral acids change the blue violet color to a blue green or green.

Determination — Hehner's Method.

To a weighed quantity of the sample, add a measured amount (more than sufficient to neutralize all mineral acid present) of tenth-normal alkali; evaporate to dryness, incinerate and titrate the ash with tenth-normal acid using methyl orange as indicator. The difference between the volume of alkali added and that of acid required, represents the equivalent of the free mineral acid in the sample.

Determination of Source.*

The principal vinegar of the United States is cider vinegar, although considerable quantities of malt vinegar are also used. The substitutes are made mainly of low-grade wine products, sugar house or glucose wastes, and wood vinegar from acetate of lime. Cheap apple jelly is sometimes added to the substitutes to give them the color, flavor, and body of cider vinegar.

Cider vinegar contains from 1.2 to 8 per cent. of solids, average about 2.5 per cent.; malt vinegar 1.75 to 6, average about 3 per cent.; spirit vinegar rarely over 0.75 per cent., average about 0.30 per cent.

The total ash in spirit and wood vinegars rarely exceeds 0.1 per cent. In fruit and malt vinegars it rarely falls below 0.2, cider vinegar averaging about 0.35 per cent.

The alkalinity of the ash, expressed as above, is, according to Frear, for cider vinegar 26 to 65, average 39; for malt vinegar 5.5; for spirit vinegar 1.1.

The flame reaction of the solids is said to be always that of potash in the case of cider vinegar, while spirit, sugar, and glucose vinegars and any which have been artificially colored show the sodium flame (Davenport-Frear).

* Cf. Frear: Bul. 65, *loc. cit.*

The optical activity of vinegar often indicates the source. Pure cider vinegar, after clarification with basic lead acetate, is lævorotatory, a 200 mm. tube giving usually a reading of — 0.5 to — 1.4 on the Ventzke scale. According to Browne, levulose is the only sugar present in properly fermented cider vinegar, the sucrose and dextrose having both disappeared in the alcoholic fermentation. Wine vinegar is also slightly lævorotatory. Vinegar from sugar house wastes is dextrorotatory before, and lævorotatory after, hydrolysis. Glucose vinegar shows dextrorotation both before and after hydrolysis. Artificial vinegars can, of course, be made lævorotatory by the addition of apple pomace.

Official Standards.

The definitions and standards established by the Secretary of Agriculture under authority of Congress are in part as follows:*

Vinegar, cider vinegar, or *apple vinegar* is the product made by the alcoholic and subsequent acetous fermentations of the juice of apples, is lævorotatory, and contains not less than 4 grams of acetic acid, not less than 1.6 grams of apple solids, and not less than 0.25 gram of apple ash in 100 c.c. The water-soluble ash from 100 c.c. of the vinegar neutralizes not less than 30 c.c. of tenth-normal acid and contains not less than 0.010 gram of phosphoric anhydride.

Wine or grape vinegar, malt vinegar, sugar vinegar, glucose vinegar, and spirit or grain vinegar are also defined with special reference to the materials from which they are prepared and must all contain at least the amount of acetic acid prescribed under cider vinegar.

References.

Allen: Commercial Organic Analysis, Volume I.

Leach: Food Inspection and Analysis.

Lunge: Chemisch-technische Untersuchungsmethoden, Band III.

Browne: The Chemical Analysis of the Apple and Some of Its Products, Bul. 58, Pennsylvania Department of Agriculture; *Journ. Amer. Chem. Soc.*, 1901, **23**, 869.

The Effects of Fermentation upon the Composition of Cider and Vinegar, *Journ. Amer. Chem. Soc.*, 1903, **25**, 16.

Frear: Vinegar, Bul. 65, Bur. Chem., U. S. Dept. Agriculture.

Leach and Lythgoe: Cider Vinegar and Suggested Standards of Purity, *Journ. Amer. Chem. Soc.*, 1904, **26**, 375.

* U. S. Dept. Agriculture, Office of the Secretary, Circular No. 13.

Van Slyke: A Study of the Chemistry of Home-made Cider Vinegar, Bul. 258, New York Agricultural Experiment Station, 1904.

FATTY ACIDS.

The fatty acids are all monobasic * and those of the common fats all contain an even number of carbon atoms in the molecule. Fatty acids containing odd numbers of carbon atoms are not widely distributed in nature, being usually characteristic of some particular fat or small group of fats. The following statement of analytical properties is based mainly upon the data given by Lewkowitsch.†

ACIDS OF THE SERIES $C_nH_{2n}O_2$.

Butyric acid, $C_4H_8O_2$, occurs ‡ in butter and in very small quantity in a few other fats. It is a mobile liquid, mixing in all proportions with water, alcohol, and ether. It boils without decomposition at 162° and is readily volatile with steam. Specific gravity at 20°, 0.959.

Caproic acid, $C_6H_{12}O_2$, occurs in butter and cocoanut fat. It is a rather oily liquid of unpleasant odor, not miscible with water but somewhat soluble in it and volatile with steam. Boiling point about 200°. Specific gravity at 20°, 0.924.

Caprylic acid, $C_8H_{16}O_2$, occurs in cocoanut oil, butter, and human fat. In the cold it crystallizes in leaflets which melt at 16.5°. It boils at 237° and is volatile with steam. One part dissolves in 400 parts of boiling water from which it separates almost completely on cooling. It is readily soluble in alcohol and ether. Specific gravity at 20°, 0.910.

Capric acid, $C_{10}H_{20}O_2$, has been found chiefly in cocoanut oil, butter, and the fat of the spice bush, *Lindera benzoin*. It melts at 31.3°, boils at 270°, and distils with steam. Soluble in about 1,000 parts of boiling water; almost insoluble in cold water; soluble in alcohol and ether.

Lauric acid, $C_{12}H_{24}O_2$, occurs abundantly in the fat of the seeds of *Lindera benzoin*, and in smaller proportions in butter, cocoanut fat, palm oil, laurel oil, and the nut oil of the California bay tree. Lauric acid melts at 43.6° and cannot be distilled at atmospheric pressure without decomposition. It is practically insoluble in cold

* For a possible exception see Gietel and Want: *Journ. prakt. Chem.*, 1900, 61, 151.

† Oils, fats, and waxes, third edition.

‡ These statements refer to the occurrence of the acids as esters rather than in the free state

water, slightly soluble in boiling water and appreciably volatile with steam. Specific gravity at 20°, 0.883.

Myristic acid, $C_{14}H_{28}O_2$, is found in nutmeg butter, dika fat, butter, cocoanut oil, lard, and many other fats, as well as in spermaceti and wool wax. It crystallizes in leaflets which melt at 53.8°. Myristic acid is insoluble in water and only very slightly volatile with steam. It is not readily soluble in cold alcohol.

Palmitic acid, $C_{16}H_{32}O_2$, occurs in nearly all solid fats and non-drying oils as well as in several waxes including spermaceti and beeswax. It melts at 62.6° and solidifies on cooling to a scaly crystalline mass. It is insoluble in water and not readily soluble in cold 95 per cent. alcohol, but dissolves in about 10 parts of cold absolute alcohol.

Stearic acid, $C_{18}H_{36}O_2$, is found in most fats and occurs most abundantly in those having high melting points. It crystallizes in leaflets which melt at 69.3°. It is less soluble in alcohol than palmitic acid, requiring about 40 parts of absolute alcohol in the cold. It dissolves readily in ether, benzol, carbon bisulphide, or hot alcohol.

Arachidic acid, $C_{20}H_{40}O_2$, occurs in arachis (peanut) oil and has been obtained in very small quantities from several other fats Arachidic acid is distinguished from all its lower homologues by its insolubility in cold alcohol. It dissolves freely in hot alcohol but on cooling separates almost completely as needles or crystalline scales, which melt at 77° to 78°.

Behenic acid, $C_{22}H_{44}O_2$, *lignoceric acid*, $C_{24}H_{48}O_2$, and an isomer of the latter, *carnaübic acid*, occur respectively in oil of ben, arachis oil, and carnaüba wax.

Cerotic acid, $C_{26}H_{52}O_2$, and *melissic acid*, $C_{30}H_{60}O_2$, are found in the free state in beeswax.

The change in properties of these acids, as the molecular weight increases, is noticeably regular. The melting- and boiling-points rise while the specific gravities and solubilities decrease. In general the properties of the glycerides and other esters vary in the same way as those of the free acids.

With the exception of caproic, all of the acids of this series, occurring in natural fats, are believed to be of the "normal" (straight chain) structure.

Acids of the Series $C_nH_{2n-2}O_2$.

These acids are unsaturated. Each molecule contains one ethy-

lene linkage or double bond and is, therefore, capable of taking up by direct addition two atoms of halogen or one molecule of hydrobromic acid to form a saturated compound. Careful oxidation in the presence of moisture results in the formation of the corresponding dihydroxy-compounds. The unsaturated acids have, as a rule, lower melting points than the saturated acids containing the same number of carbon atoms, and are therefore found more largely in oils and soft fats. Only the more important members of the series will be considered here.

Hypogæic acid, $C_{16}H_{30}O_2$, obtained from arachis (peanut) oil, melts at 33°, but is converted by the action of nitrous acid into the isomeric gaidic acid which melts at 39°. *Phycetoleic acid*, isomeric with hypogæic, is obtained from sperm oil and seal oil. It melts at 30° and is not changed by nitrous acid.

Oleic acid, $C_{18}H_{34}O_2$, occurs in nearly all fats and fatty oils. It is an oily liquid which solidifies at 4° and melts at 14°. Nitrous acid converts oleic acid into the isomeric elaidic acid which is a crystalline solid melting at 44.5° (Lewkowitsch).

Erucic acid, $C_{22}H_{42}O_2$, found in rape seed and mustard seed oils, melts at 33° to 34°. By the action of nitrous or sulphurous acid it can be converted into brassidic acid, melting at 65°. This change, however, takes place less readily than the corresponding conversion of oleic acid into elaidic acid.

The gradual change in properties with increasing molecular weight, noticed in the saturated acids, is not apparent in this series, doubtless because the known acids of the series differ as regards the position of the double bond and are therefore not strictly similar in constitution. The property of changing to solid isomers under the influence of nitrous acid is characteristic of the acids of this series and furnishes a means of testing for them in fatty oils. Any of the latter which contain large amounts of these acids become solid or semi-solid on treatment with nitrous acid. This is known as the *elaidin test* and is sometimes useful in the preliminary examination of oils, but has been shown to be less reliable than was formerly supposed.

An important characteristic of the unsaturated acids is the solubility of the lead soaps in ether. Muter's method for the separation of saturated and unsaturated fatty acids, is to precipitate the mixture of acids as lead soaps and wash with ether. While this method is not strictly quantitative, it is probably the best which has been devised for the purpose.

Acids of the Series $C_nH_{2n-4}O_2$.

The acids of this series unite with four atoms of bromine or iodine and absorb oxygen on exposure to the air.

Linoleic acid, $C_{18}H_{32}O_2$, is the only important member of the series. It is widely distributed occurring most abundantly in the "drying oils," so called because they are oxidized to solids on exposure to air. While especially characteristic of the drying and semi-drying oils, linoleic acid is also found in nondrying oils and in small quantity in some of the solid fats. It absorbs oxygen from the air so readily as to interfere seriously with ordinary methods of purification and examination. Its physical properties are therefore not well known but it has been shown to have a higher specific gravity than oleic acid and a much lower melting point since it does not solidify at — 18°. Linoleic acid is not changed by nitrous acid. Lead linoleate is soluble in ether.

Acids of the Series $C_nH_{2n-6}O_2$.

Linolenic acid, $C_{18}H_{30}O_2$, is the only member of this series which has been obtained in the free state. It is a colorless oil which absorbs oxygen very rapidly from the air, at the same time becoming dark brown. The purest preparations of the acid which have been described absorbed 242 to 245 per cent. of iodine. The pure acid should absorb six atoms or 274 per cent. of iodine. Linolenic acid has not been solidified. Its specific gravity is greater than that of linoleic acid. The lead soap is soluble in ether. Linolenic acid occurs in considerable quantity in linseed oil. By oxidizing linseed oil acids with alkaline permanganate Hazura obtained two acids of the formula $C_{18}H_{30}(OH)_6O_2$, linusic and isolinusic acids, and hence inferred the presence of an isolinolenic acid in linseed oil. Jecoric acid, isomeric with linolenic acid, is reported by Fahrion * as existing in sardine oil. Since the oils of fish and other marine animals do not dry like the vegetable oils having the same iodine absorbing power, it is probable that the highly unsaturated acids of the former oils are in general isomeric, rather than identical, with linolenic acid. Some of the fish oils are thought to contain acids of the series $C_nH_{2n-8}O_2$

Saturated Hydroxy-Acids.

When any of the unsaturated acids occurring in vegetable oils is carefully oxidized in alkaline solution by means of potassium

* Chem. Ztg., 1893, 17, 521.

permanganate, hydroxyl is added until the molecule becomes saturated. Thus oleic acid yields dihydroxystearic acid, $C_{18}H_{34}(OH)_2O_2$, linoleic acid yields sativic acid, $C_{18}H_{32}(OH)_4O_2$, and linolenic acid yields linusic acid, $C_{18}H_{30}(OH)_6O_2$. Similar changes in the unsaturated acids may take place when their glycerides are exposed to the air. Small amounts of saturated hydroxy-acids are, therefore, likely to be present in fatty oils which have been kept for some time in partially filled bottles or otherwise exposed to atmospheric oxidation. Only two acids of this series have as yet been found in nature. Juillard* found about 1 per cent. of dihydroxystearic acid in castor oil and Browne† the same quantity in butter fat. A dihydroxy-acid of the formula, $C_{30}H_{60}O_4$, is said to occur in wool wax‡ and is called lanocerinic or lanoceric acid.

Hydroxy-Acid of the Series $C_nH_{2n-2}O_3$.

Ricinoleic acid, $C_{18}H_{34}O_3$, the only important member of this series, occurs in large quantity in castor oil. It is a very viscous liquid of much higher specific gravity than oleic or linolic acid. According to Juillard§ the pure acid melts at 4°–5°, and is miscible with alcohol and ether in all proportions. Ricinoleic acid is dextrorotatory. The position of the asymetric carbon atom, as well as of the double bond, is shown by the following formula‖

$$C_6H_{13}\cdot CH(OH)\cdot CH_2\cdot CH : CH\cdot (CH_2)_7\cdot COOH.$$

Ricinoleic resembles oleic acid in its chemical reactions. It absorbs two atoms of bromine or iodine. By treatment with permanganate in alkaline solution two hydroxyl radicals are added. By treatment with nitrous acid, ricinoleic acid is converted into the solid isomer, ricinelaidic acid. Lead ricinoleate is easily soluble in ether.

Separation of Fatty Acids.

For the analytical separation of saturated from unsaturated fatty acids, Muter's method, based on the solubility of the lead soaps of the latter in ether, is generally used. In order to determine the constituents of a mixture of homologous acids it is usually necessary to

* *Bull. Soc. Chim.*, 1895, [3] 13, 238.

† *Journ. Amer. Chem. Soc.*, 1899, 21, 817.

‡ Darmstaedter and Lifschütz: *Ber. deut. chem. Ges.*, 1896, 29, 1476.

§ *Bull. Soc. Chim.*, 1895, [3], 13, 240.

‖ Goldsobel: *Ber. deut. chem. Ges.*, 1894, 27, 3121. Kasansky: *Journ. prakt. Chem.*, 1900, 62, 363.

fraction the mixture repeatedly either by distillation, precipitation or crystallization, until each fraction contains only two acids. The proportions of the two constituents can then be found by determining the mean molecular weight of the mixture. Such methods are outlined by Allen (Commercial Organic Analysis, 3d Ed., I., 485–492; II., 240–246) and by Browne, in a paper on the chemistry of butter fat, *Journ. Amer. Chem. Soc.*, 1899, **21**, 807.

CHAPTER IX.

Oils, Fats, and Waxes — General Methods.

All glycerides of fatty acids are properly known as fats. As a matter of convenience those fats which are liquid at ordinary temperatures are commonly called fatty oils. Fats and fatty oils, therefore, constitute a definite group of compounds, the glyceryl esters of the fatty acids.

Waxes are esters of fatty acids with monatomic alcohols of high molecular weight. Most waxes are solid at ordinary temperatures and the term is sometimes applied to other solids of similar physical properties, solid hydrocarbons, for example, being frequently called mineral waxes.

The term oil has no strict chemical significance, being applied not only to liquid fats, but also to substances, such as mineral and essential oils, which are similar in some physical properties but entirely different in constitution. The mineral oils are conveniently treated in connection with the fatty oils in works on technical analysis, because on account of their similar physical properties they may for certain uses be mixed with, or substituted for, the fatty oils and are sometimes found as adulterants of the latter. The same is true of some of the essential oils, notably rosin oil and turpentine.

The methods given in this chapter are described and discussed with special reference to the analysis of solid and liquid fats. In most cases, however, they are also applicable to waxes, non-fatty oils, and technical mixtures.

PROPERTIES OF FATS AND FATTY OILS.

Refined fats and fatty oils are usually light yellow to colorless. Vegetable oils are sometimes tinged green by the presence of chlorophyll. Crude oils are often reddish or even dark brown. The characteristic colors, odors, and flavors of natural fats are due to small quantities of substances other than glycerides, and therefore become less perceptible the more thoroughly the oil is refined. It is believed that all of the natural glycerides except butyrin, if obtained absolutely pure, would be colorless, tasteless, and odorless.

The natural glycerides are all lighter than water and insoluble in it. They can take up a very small amount of water, which is given off as steam on heating. The quantity of water which can be held by a fatty oil without causing turbidity is, however, negligible, so that for practical purposes the fatty oils may be considered as immiscible with water.

They dissolve readily in ether, carbon bisulphide, chloroform, carbon tetrachloride, and benzol, and mix with each other in all proportions. With the exception of castor oil and a few other oils characterized by a large proportion of hydroxy-acids, they are sparingly soluble in alcohol or acetic acid, but dissolve readily in petroleum ether and mix in all proportions with mineral oils. Castor oil is readily soluble in alcohol or acetic acid and not readily miscible with petroleum ether or mineral oils.

The glycerides do not distil without decomposition. When decomposed by heating they give off acrolein which is readily recognized by its characteristic irritating odor.

A simple triglyceride is one in which the three acid radicals are of the same kind. A glycerol ester containing the radicals of two or three different fatty acids is known as a mixed glyceride. Both simple and mixed glycerides have been isolated from natural fats and certain physical differences in fats which contain practically the same acids are now attributed to the presence of mixed glycerides. For discussions of simple and mixed triglycerides, see Lewkowitsch's Oils, Fats and Waxes, 3d Ed., Chapter I., and recent papers by Hansen,* Holde,† and Kreis and Hafner.‡

ANALYTICAL METHODS.

The object of an ordinary fat or oil analysis is not so much to separate individual constituents as to determine certain chemical and physical properties which are fairly constant for each variety when pure and are therefore frequently called analytical constants. All solid and liquid fats being essentially mixtures of triglycerides, any differences in chemical and physical properties (except such physical variations as are due to mixed glycerides) must be attributed mainly to the presence of different fatty acids, or of the same acids in different proportions.

* Ueber das Vorkommen gemischter Fettesaüre-Glyceride in theirischen Fette. Dissertation, Rostock, 1902; *Arch. Hygiene*, 1902, 42, 1.

† *Ber. deut. chem. Ges.*, 1902, 35, 4306.

‡ *Ber. deut. chem. Ges.*, 1903, 36, 1123, 2766; *Ztschr. Unters. Nahr.-Genussm.*, 1904, 7, 641.

The principal differences to be expected are: (1) In the mean molecular weight of the acids present or the relative proportions of acids of high and those of low molecular weight; (2) in the relative number of "double bonds" depending upon the proportions of acids of the stearic, oleic, linoleic, and linolenic types; (3) in the proportion of hydroxy-acids present.

Some of the analytical "constants" express direct measures of one of these three properties. Others, especially the physical constants, are influenced by variation in any of these three directions and therefore express no one chemical property but a resultant of all. The "constants" most used may be grouped on this principle as follows:

1. (*a*) Measuring the mean molecular weight.—Saponification or Koettstorfer number. (*b*) Measuring the proportion of acids of high or of low molecular weight.— Hehner number, Reichert-Meissl number.

2. (*a*) Measuring the proportion of unsaturated acids (number of "double bonds").—Hübl number and other halogen absorption numbers. (*b*) Depending mainly upon the proportion of unsaturated acids.— Thermal reactions with bromine or sulphuric acid, Maumené number,

3. Measuring the hydroxyl radical and therefore, depending mainly upon the presence of hydroxy-acids.— Acetyl number.

4. Influenced by all of the above properties.— Specific gravity, index of refraction, melting point, "titer test," viscosity, solubilities.

The Saponification or Koettstorfer Number.*

The saponification or Koettstorfer number is the number of milligrams of potassium hydroxide consumed in the complete saponification of one gram of the fat or wax; or, in other words, it is ten times the percentage of potassium hydroxide required to neutralize the total fatty acids in the sample, whether free or in the form of esters.

Reagents.— 1. Standard solution of hydrochloric acid preferably half-normal.

2. Alcoholic potash solution containing 40 grams of potassium hydroxide per liter of purified 95 per cent. alcohol. In the prep-

* Koettstorfer: *Ztschr. anal. chem.*, 1879, 18, 199, 431. Reprinted in Ephraim's Originalarbeiten über Analyse der Nahrungsmittel, Leipzig, 1895.

aration of this solution the best available potassium hydroxide (purified by alcohol) should be dissolved in alcohol which has been purified by redistillation over caustic alkali. The solution must be clear when used.

3. As indicator a 1 per cent. solution of phenolphthalein in purified 95 per cent. alcohol.

Determination. — Weigh 4 to 5 grams of the fat or oil in a 250 c.c. Erlenmeyer flask, add 50 c.c. of the alcoholic potash solution, connect with a reflux condenser and boil for thirty minutes, or until the oil is completely saponified, so that the liquid in the flask appears homogeneous and clear. At the same time measure 50 c.c. of the alcoholic potash solution into an empty flask of the same size and shape, connect with a similar reflux condenser and boil for the same length of time as in the case of the solution containing the sample. Cool the flasks and titrate each with the standard hydrochloric acid, using 1 c.c. of the phenolphthalein solution as indicator. The difference between the titrations gives a measure of the potassium hydroxide consumed in saponifying the sample.

Notes. — When ordinary alcohol is used for the potassium hydroxide solution, the latter rapidly turns brownish so that the final titration is difficult. Alcohol which has been treated with potassium hydroxide, allowed to stand for one to two weeks and then redistilled, gives a much more permanent solution. According to Gill scarcely any darkening of the solution occurs if it is kept under an atmosphere of hydrogen. Great care must be exercised to measure exactly the same quantity of the alkaline solution into each flask, and to treat the blank solution in exactly the same way as that containing the sample, so that any loss of alkalinity due to absorption of carbon dioxide from the air, or to the possible action of the alkali on the solvent, may be the same in each case. If sulphuric acid were used in place of hydrochloric for the final titration a precipitate of potassium sulphate would be formed in the alcoholic solution, thus impairing the delicacy of the end reaction.

In order to avoid the changes which may occur in the alkali solution on boiling, Henriques* recommends that the saponification be conducted in the cold. From 3 to 4 grams of oil are mixed with 25 c.c. of petroleum ether and 25 c.c. of normal alcoholic potash and allowed to stand over night at room temperature, when the saponification is said to be complete.

* *Ztschr. angew. Chem.*, 1895, 721; 1896, 221, 423.

The Saponification Equivalent.

The results obtained as described are sometimes expressed in terms of the *saponification equivalent.* This is the weight of fat which reacts with the molecular weight of sodium or potassium hydroxide; or, in other words, the number of grams of fat which would be saponified by one liter of normal alkali. Comparing this with the definition of the *saponification* (or Koettstorfer) *number* it will be seen that these two values express the same property in reciprocal terms and that the product of the two values is always equal to the number of milligrams of potassium hydroxide in a liter of normal solution, viz. 56,158.

Hence

$$\text{Saponification equivalent} = \frac{56{,}158}{\text{saponification number}}$$

$$\text{Saponification number} = \frac{56{,}158}{\text{saponification equivalent}}$$

For a sample consisting entirely of triglycerides the saponification equivalent would be exactly one-third of the mean molecular weight of these glycerides.

Acid and Ester Numbers.

The *acid number* of a fat or wax is the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in one gram of substance.* The *ester number* is the difference between the saponification number and the acid number and therefore shows the amount of alkali consumed in the saponification of esters.

To determine the acid number, shake 4 to 5 grams of the sample with 50 c.c. of carefully neutralized alcohol and titrate with tenth-normal or half-normal alkali, using phenolphthalein as indicator. As the oil itself mixes but slightly with alcohol, it is necessary toward the end of the titration to shake thoroughly after each addition of alkali to secure complete extraction of the fatty acid from the oily layer.

* The acidity of a sample of oil or fat is not always expressed as the "acid number." Frequently it is recorded in terms of the equivalent percentage of free oleic acid, "acidity as oleic," and sometimes as "degrees of acidity." The latter term indicates the number of c.c. of normal caustic alkali required to neutralize the free acids in 100 grams of the fat.

The Hehner Number.

The Hehner number is the percentage of insoluble fatty acids obtainable from a fat.

As the determination is ordinarily made, the unsaponifiable matter present in the fat is weighed with the insoluble acids. The great majority of fats and fatty oils have Hehner numbers between 94.5 and 96. Butter fat has a lower Hehner number and the determination of this "constant" is of value chiefly in testing the purity of butter. The detailed description of the process will therefore be given in the chapter on butter analysis.

The Reichert-Meissl Number.

The Reichert-Meissl number is the number of cubic centimeters of tenth-normal caustic alkali required to neutralize the soluble volatile acids obtained from 5 grams of a fat by the Reichert distillation process.

This number serves as a comparative measure of the acids of low molecular weight. Its principal use is in the examination of butter fat and the detailed description will be given in that connection. The Reichert number is about one-half the Reichert-Meissl number, Reichert having originally recommended the use of 2.5 grams of fat. Among the common oils and fats the Reichert-Meissl numbers are usually less than 1.0. Butter fat has a high Reichert-Meissl number and as this determination is used principally in the examination of butter, it will be described in the chapter on butter analysis.

The Iodine or Hübl Number.

The iodine or Hübl number is the percentage of iodine (or of iodine chloride or bromide expressed in terms of iodine) absorbed by the sample.

This number gives a quantitative measure of the unsaturated fatty acids (or of the "number of double bonds") in a fat or wax.

Mills, Snodgrass and Akitt were probably the first to make systematic use of the halogen absorbing power in fat analysis. In their experiments* the oil or fat to be tested was dissolved in carbon tetrachloride and titrated with a standard solution of bromine in carbon tetrachloride as long as the bromine was absorbed. At

* *Journ. Soc. Chem. Ind.*, 1883, 2, 435; 1884, 3, 366.

about the same time, Hübl published* a method based upon the use of iodine in an alcoholic solution of mercuric chloride which was so carefully worked out in all of its details that the original form of the process is still used in many laboratories in preference to any of the modifications which have been proposed. Recently, however, the Wijs† and the Hanus‡ modifications have been largely used, and it is probable that they will gradually replace the Hübl process. These three methods will be given here. The bromine absorption method as developed by McIlhiney§ can be used in place of the iodine methods, but is more especially adapted to the examination of linseed oil for rosin oil or rosin, and will be referred to in that connection in the next chapter.

Method of Hübl.

Reagents. — 1. Iodine solution. Dissolve 26 grams of pure iodine in 500 c.c. of 95 per cent. alcohol. Dissolve 30 grams of mercuric chloride in 500 c.c. of alcohol of the same strength. Mix the two solutions at least 12 hours before using. As this solution is expensive and does not keep well, no more than a week's supply should be made at one time.

2. Standard solution of sodium thiosulphate. Dissolve 24 grams of the crystallized salt in a liter of water, allow to stand at least 24 hours and then determine the strength of the solution in terms of iodine. While any of the well-known methods may be used, it is convenient to standardize the thiosulphate solution as follows:

Weight 3.8694 grams of pure dry potassium dichromate, dissolve in water and dilute to 1000 c.c. In a well-filled tightly-stoppered bottle, this standard solution of dichromate can be kept indefinitely without deterioration. Each c.c. of this solution is equivalent to 0.01 gram iodine. Mix 25 c.c. of a 15 per cent. potassium iodide solution with 5 c.c. of hydrochloric acid, add 50 c.c. of the dichromate solution, and titrate the liberated iodine by means of the thiosulphate solution, observing procedure and precautions described below. Calculate the amount of iodine consumed by each c.c. of the thiosulphate solution. As a precaution the strength of either the dichromate or the thiosulphate solution should also be determined by an independent method.

* *Dingl. polyt. Journ.*, 1884, 253, 281. Reprinted by Ephraim, *loc. cit.*

† *Ber. deut. chem. Ges.*, 1898, 31, 750.

‡ *Ztschr. Unters. Nahr.-Genussm.*, 1901, 4, 913.

§ *Journ. Amer. Chem. Soc.*, 1884, 16, 245; 1899, 21, 1084; 1902, 24, 1109.

3. An approximately 15 per cent. solution of pure potassium iodide in cold, recently boiled, distilled water.

4. Freshly prepared starch solution, 1 part starch to 200 parts of water, for use as indicator.

5. Pure chloroform.

6. Cold, recently boiled, distilled water.

Determination. — Thoroughly clean and dry two or more thin Erlenmeyer flasks, of the form made for this purpose, having accurately ground glass stoppers and flaring mouths which form a gutter between the stopper and the lip. Into one of these flasks weigh such an amount of the sample as will absorb between 0.3 and 0.4 gram of iodine * and add 10 c.c. of chloroform. When the sample has completely dissolved, add 25 c.c. or 30 c.c. of the mixed iodine solution, stopper carefully, fill the gutter around the stopper with potassium iodide solution to guard against loss of iodine, shake gently, and allow the flask to stand in a cool dark closet for 3 to 20 hours according to the nature of the sample. In another clean dry flask of the same size and form make a blank determination using the same amounts of chloroform, iodine solution, and potassium iodide. Allow the two flasks to stand side by side for the same length of time. When the absorption is complete, lift the stopper in such a way that its lower surface will be washed by the iodide solution from the gutter; add 100 c.c. of cold, recently boiled, distilled water and 20 c.c. more of the potassium iodide solution, washing down the sides of the flask with the latter. In case a red precipitate of mercuric iodide appears, add more potassium iodide until the precipitate is dissolved. Titrate the excess of iodine at once by means of the standard thiosulphate solution. The latter may be run in rapidly until the iodine is nearly consumed and the solution is only light yellow; then add 2 c.c. of the starch solution and finish the titration carefully but without delay. As the end point is approached, stopper the flask quickly after each addition of thiosulphate and shake vigorously to ensure thorough and rapid mixing of the contents. The end point should be sharper than in standardizing since in this case there is no green color due to chromium and the solution passes at once from blue to nearly colorless. The difference between the volume of thiosulphate solution required for the blank test and that required for the solution containing the sample gives a meas-

* See iodine numbers in table at the end of this chapter.

ure of the iodine absorbed by the latter. Calculate the iodine absorbed in terms of percentage of the original weight of sample.

Notes. — Most of the difficulties which are met in using this method are due to impure reagents or failure to observe carefully the conditions worked out by Hübl. Probably the most important sources of error are: (1) The use of impure chloroform or water containing dissolved air causing a liberation of iodine from the potassium iodide; (2) loss of iodine from the use of vessel with imperfectly fitting stopper or from titrating at too high temperature or with too much exposure to air; (3) deterioration of the iodine solutions due chiefly to impurities in the alcohol or too high temperature; (4) variations in the excess of iodine over that absorbed; (5) variations in the length of time allowed for the reaction.

The small amount of oil needed for this determination can conveniently be drawn from near the center of the sample bottle by means of clean glass tubing of about 2 mm. internal diameter. Use a piece of thin tubing like a pipette, wiping it free from oil on the outside and allowing it to deliver drop by drop into the weighed flask which should then be stoppered and reweighed at once. If more than one sample of oil is to be tested, delays can be avoided by having a number of pieces of the tubing cleaned and dried in advance so that each can be rejected after using it for one sample.

The best results are obtained by using such proportions of oil and of iodine solution as to have present from two to three times the amount of iodine which will be absorbed. With samples which absorb only small amounts of iodine the reaction is probably complete in two or three hours, but with linseed and similar oils it is necessary to allow the iodine solution to act longer. It has been claimed that several hours standing introduces an error through the deterioration of the iodine solution in the blanks, but this need not be feared if the reagents are pure and the flasks tightly stoppered and kept in a cool dark place. Unless it is certain that a shorter time will be sufficient it is well to allow the determinations to stand over night. The form of vessel to be used for the test is, of course, immaterial so long as loss of iodine is avoided. Some prefer to weigh the sample on a small watch glass and place the latter with the sample in a wide-mouth glass stoppered bottle. A blank test must be run with each determination, or if several samples are treated at once there should be at least two or three blanks.

For discussion of the theory of the action of Hübl's solution see Lewkowitsch's Oils, Fats, and Waxes, or Gill's Oil Analysis.

Method of Wijs.

Wijs found that a solution of iodine monochloride in glacial acetic acid acts in the same manner as Hübl's solution, but more quickly. Moreover, the reagent is much more stable than that of Hübl, so that the same solution can be used for several months and blank tests are not so frequently required.

Reagents.— 1. Glacial acetic acid. This must contain not over 0.5 per cent. of water and no impurity capable of reducing potassium dichromate. Test by adding a small amount of a solution of dichromate in sulphuric acid and warming on a water-bath; no green tinge should appear.

2. Iodine chloride solution. Dissolve 12.5 to 13 grams of iodine in a liter of the glacial acetic acid, warming gently to aid solution, if necessary. Cool, withdraw 25 c.c., add potassium iodide solution and determine the iodine content by titration with standard thiosulphate; into the remainder of the solution pass a current of chlorine until the deep iodine color changes to an orange yellow, showing that the conversion of iodine to iodine monochloride is complete. A portion of the solution titrated with thiosulphate should now show twice the original halogen content. In case an excess of chlorine is found, a weighed amount of iodine equivalent to this excess may be dissolved in the solution.

3. Standard solution of sodium thiosulphate, as in the method of Hübl.

4. Pure chloroform, potassium iodide, starch solution, and distilled water as described under Hübl's method.

Determination.— The determination is carried out in exactly the manner described for the Hübl method except that 10 c.c. of the potassium iodide solution are sufficient and a much shorter time is required for the reaction. With non-drying oils the addition of iodine chloride is complete in 15 minutes. Ordinarily the solution should be titrated after standing one hour.

Notes.—As the solution of iodine chloride in acetic acid is more viscous and has a higher coefficient of expansion than ordinary aqueous solutions, the portions added must be measured as carefully as possible, allowing a uniform time for the burette to drain, and observing that the temperature does not vary more than three or

four degrees. With these precautions it is not always necessary to make a blank test with each determination after a sufficient number of such tests have been made to show that the solution is not changing appreciably in strength.

Method of Hanus.

Hanus suggested that Wijs' method be modified by the use of iodine bromide in place of iodine chloride. As an excess of iodine does no harm, the preparation of the reagent is simpler than in the preceding method.

The reagents required are the same as for the Wijs method except that the iodine bromide solution is prepared by dissolving 13.2 grams of iodine and 3 c.c. of bromine in a liter of glacial acetic acid. The iodine may be dissolved first in the greater part of the acid, heating to aid solution; the bromine is added after cooling the solution and the volume then brought to a liter.

The manipulation is the same as in the Wijs method, but as the reaction is not quite so rapid an hour should be allowed in all cases. It is well to make the determination in duplicate, allowing more time in one case than in the other. After adding the potassium iodide solution shake thoroughly before adding water.

Comparison of the Hübl, Wijs, and Hanus Methods.

Wijs based his modification on the belief that iodine chloride is the active substance in Hübl's solution and that the more stable solution of iodine chloride in acetic acid should give the same theoretical results with greater certainty. That higher results were often obtained by his method Wijs attributed to the deterioration or incomplete action of the Hübl solution as ordinarily prepared. Lewkowitsch * confirms this, stating that when the Hübl method is carried out under the best conditions the results of the two methods agree.

Tolman and Munson, † however, in an extended comparison of the three methods almost invariably obtained higher results by the Wijs than by the Hübl method. Hanus' method gave intermediate results, usually agreeing quite closely with the Hübl numbers. Similar results on a smaller number of samples had previously been published by Hunt ‡ and have since been obtained by W.

* *Analyst*, 1899, **24**, 259.

† *Journ. Amer. Chem. Soc.*, 1903, **25**, 244.

‡ *Journ. Soc. Chem. Ind.*, 1902, **21**, 454.

G. Tice.* For oils having iodine numbers below 100, the three methods can be used interchangeably as the differences in results will rarely exceed 1.5 units which is only about one-tenth of the variation which occurs among pure oils of the same species. In applying the Wijs solution to oils having much higher iodine numbers it is to be remembered that results as much as 10 units in excess of these given by Hübl's solution will sometimes be obtained.

The method of Hübl is "official" in the United States but that of Hanus has been adopted by the Association of Official Agricultural Chemists as a provisional optional method for the examination of edible oils and fats. The method of Wijs is more commonly used in England and is recommended in preference to the Hanus method by Lewkowitsch † and Archbutt, ‡ the latter pointing out especially that the Wijs solution gives approximately the theoretical iodine number for turpentine (which is often mixed with fatty oils) while that of Hanus gives much lower results.

In comparing analytical results with the numbers found in "tables of constants" it should be remembered that the latter are based in part upon results obtained (not always under the best conditions) by Hübl's method, and in part upon later results determined according to Wijs. Such tables tend to show a greater range than would be found by the use of either method alone, this being especially true of the oils having high iodine numbers.

Maumené Number — Specific Temperature Reaction.

Long before the introduction of any of the halogen absorption methods Maumené § tested olive oil for adulterants such as poppy-seed oil by mixing fixed volumes of oil with strong sulphuric acid and observing the rise in temperature which is much greater with seed oils than with olive. The rise of temperature, expressed in degrees C., which occurs on mixing 10 c.c. of strong sulphuric acid with 50 grams of oil is commonly known as the Maumené number. Thomson and Ballantyne || pointed out the discrepancies which may be introduced through variations in the strength of the acid used, and showed that they can be largely avoided by comparing the rise observed in the case of an oil with that

* In the Havemeyer Laboratory, Columbia University.

† Oils, Fats and Waxes (3d Ed.), I., 252.

‡ *Journ. Soc. Chem. Ind.*, 1904, 23, 306.

§ *Compt. rend.*, 1852, 35, 572.

|| *Journ. Soc. Chem. Ind.*, 1891, 10, 234.

shown by water under the same conditions, the latter being taken as 100. The result thus obtained is known as the specific temperature reaction or specific Maumené number. Thus if 50 grams of water mixed with 10 c.c. of sulphuric acid showed a rise of 40° and 50 grams of an oil showed under the same conditions a rise of 36° the specific Maumené number of the oil would be 90.

With fresh fatty oils the rise of temperature depends mainly upon the presence of glycerides of the unsaturated acids and the Maumené and Hübl numbers are therefore roughly proportional. This relation, however, is not sufficient to permit of the determination of the Maumené in place of the iodine number except for rough work or as a preliminary test. The greatest value of this temperature reaction lies in the fact that as oils become altered by absorption of oxygen from the air, the Maumené numbers increase while the iodine numbers decrease. The significance of this relation is more fully explained in the next chapter.

Apparatus and Reagents. — A deep beaker of 150 to 200 c.c. capacity should be used for this test and should be so jacketed as to prevent a rapid loss of heat. This is done by placing it in a larger beaker or a metal cup and filling the space with asbestos or other dry porous material. If a new nest of beakers is at hand the test can be made in one of the smaller beakers using the remainder of the nest with the packing intact as a jacket. The insulation should be sufficient to prevent the outer vessel from becoming perceptibly warm when a test is made. The only reagent required is strong sulphuric acid which can be added either from a burette or (more satisfactorily) from a 10 c.c. pipette. For observing the rise in temperature use a thermometer graduated in degrees on which the readings can be taken with accuracy to 0.2 degree.

Determination. — The oils to be tested, the acid and apparatus to be used, and the distilled water which is to serve for comparison must all have the same initial temperature, which should be between 20° and 24°. This will usually be the case if they have stood side by side at room temperature for several hours. Measure 50 c.c. of water into the beaker, introduce the thermometer and note the temperature; add 10 c.c. of the acid, stirring thoroughly with the thermometer so that the solution is kept well mixed and the temperature rises steadily. At intervals of a few seconds bring the bulb of the themometer to the center of the solution and

observe the temperature. Record the highest reading found. When the mixture in the beaker has reached its maximum temperature it should be rejected at once to avoid unnecessary warming of the apparatus, since the initial temperature must be restored before beginning another test. After the rise with water has been found by duplicate determinations which do not differ by more than 0.4°, dry the beaker thoroughly, weigh into it 50 grams of oil (within 0.05 gram), and treat with 10 c.c. of acid in exactly the same manner. The mixture often becomes very viscous, requiring vigorous stirring to ensure a uniform temperature. In reporting results give the actual rise observed with oil and with water as well as the specific temperature reaction.

Notes. — By the use of a pipette having a fine outlet requiring 30 to 60 seconds for the 10 c.c. of acid to flow into the beaker, more thorough mixing becomes possible and better results are secured. In order to avoid trouble in cleaning the beaker it should be emptied and wiped with dry cotton waste or porous paper while still warm. The acid used must be protected from unnecessary exposure to air as it readily absorbs moisture to an extent sufficient to cause an appreciably lower temperature reaction. In testing edible and lubricating oils the strongest available sulphuric acid should be used. In the case of drying oils and fish or other marine animal oils, the addition of such strong acid to the undiluted oil causes violent frothing and decomposition. This may be avoided * by the use of sulphuric acid of such strength as to give a rise of 35° when added to water under the conditions to be used in testing the oil. An important modification of this test has been proposed by Mitchell.†

The Acetyl Number.

The acetyl number is the number of milligrams of potassium hydroxide required to neutralize the acetic acid obtained by saponification of one gram of the acetylated fat or wax.

It indicates the proportion of alcoholic hydroxyl groups in the original substance. If the latter consists essentially of triglycerides, the acetyl number serves as a measure of the hydroxy-acids present. Free alcohols, if present, increase the acetyl numbers. Lew-

* Sherman, Danziger and Kohnstamm : *Journ. Amer. Chem. Soc.*, 1902, 24, 266.

† *Analyst*, 1901, 26, 169. See also Sherman and Falk : *Journ. Amer. Chem. Soc.*, 1903, 25, 713.

kowitsch finds that free fatty acids of the stearic series may also react in such a way as to increase the apparent acetyl numbers, and therefore prefers to acetylate the original fat or wax rather than to work with the mixed fatty acids as was previously recommended by Benedikt and Ulzer. *

The method of Lewkowitsch is essentially as follows: †

Boil 10 grams of the substance with twice its weight of acetic anhydride in a round bottomed flask under a reflux condenser for two hours; pour the resulting mixture into a large beaker containing 500 c.c. of hot water and boil for half an hour, passing a slow current of carbon dioxide through the solution to prevent bumping. Allow the mixture to separate into two layers, siphon off the water, and boil the oily layer with three successive portions of fresh water, the last of which should not react acid to litmus paper.

All free acetic acid having been removed, the acetylated fat is carefully separated from water and further dried by filtering through anhydrous paper in a drying oven.

Weigh 2 to 5 grams of the acetylated fat and saponify with a measured volume of standard alcoholic potash as in the determination of the saponification number; evaporate nearly to dryness to expel the alcohol, dissolve the soap in water and add an amount of standard sulphuric acid exactly equivalent to the alkali used for saponification. Warm gently until the fatty acids separate as a layer at the top. Filter through wet paper, wash the fatty acids with boiling water until the filtrate is no longer acid, and titrate the filtrate and washing with tenth-normal alkali, using phenolphthalein as indicator. Deduct the amount of alkali required to neutralize any soluble fatty acids in the original substance and calculate the acetic acid found, in terms of acetyl number, as defined above.

Instead of filtering and washing with water, the acetic acid can be separated from the fatty acids by distilling with steam, but this requires considerably more time than the filtration process.

In the examination of waxes the acetyl numbers show the proportional amounts of free alcohols. Fats and fatty oils contain free alcohols (cholesterol, phytosterol, etc.), but in very small amounts only, so that the acetyl numbers are low except in oils which contain hydroxy-acids. (Chapter VIII.) The acetyl number of castor oil is about 150. Other oils rarely show acetyl

* *Monatsh. Chem.*, 1887, 8, 40.

† *Journ. Soc. Chem. Ind.*, 1897, 16, 503; Oils, Fats and Waxes (3d ed.), I., 268.

1280K.
150S.
320K

1260K.
160S.
370A

320S.
350K.

numbers higher than 10, unless they have been exposed to atmospheric oxidation, in which case hydroxy-acids may have been formed from the unsaturated acids originally present.

Specific Gravity.

The specific gravities of the glycerides depend upon the fatty acids which they contain. Comparing acids of the same homologous series the specific gravity was found to decrease with increasing molecular weight; while between corresponding acids of different series it increases with the number of double bonds and of hydroxyl groups.

Fresh specimens of the same kind vary but little in specific gravity, and the determination of this property is often useful in differentiating oils, fats, and waxes and in testing them for adulterations. The determination can be made either by means of a very delicate special hydrometer, by the Westphal balance, or by one of the methods described in Chapter III. On account of the high coefficient of expansion of oils it is important that the temperature at which the specific gravity is taken be accurately known. This is conveniently accomplished by using the thermometer sinker with the Westphal balance.

Directions for the use of the Westphal balance are usually supplied with the instrument. It should always be placed upon a firm level table and very carefully adjusted before using. In setting up the instrument be sure that the leveling screw is directly beneath the arm which supports the beam. Place the latter in position and hang the sinker. Compare the height of the beam with that of the cylinder which is to contain the oil and lengthen or shorten the standard if necessary, then carefully adjust the balance by means of the leveling screw until the point projecting from the end of the beam stands exactly opposite the fixed point at the left. Nearly fill the cylinder with the oil at about 14°. Lift the sinker, place the cylinder under the end of the beam and replace the sinker so that it hangs freely in the oil. The specific gravity is now found by placing weights on the beam until the balance is restored. Make the final adjustment of the smallest weight when the thermometer in the sinker shows the desired temperature — for oils, 15.5°. The specific gravity is read directly from the position of the weights on the beam. If the largest weight is at 9, the second at 3, the third at 1, and the fourth at 5, the spe-

cific gravity of the oil is 0.9315. The readings should be made to four decimal places (*i. e.*, all four sizes of weights should be used) and the error of determination should not exceed 0.0005. By using the same sinker on the analytical balance or by weighing the oil in a pyknometer, more accurate results can be obtained. The Westphal balance is, however, sufficiently delicate for routine work if carefully used. Care must be taken that the sinker is always suspended at the same depth in the liquid under examination. The graduation of the beam should be tested to see that the spaces are all of equal length, and the results should occasionally be verified by comparative determinations with the pyknometer. In working with very viscous oils it is advantageous to use a sinker of high specific gravity.*

For the determination of specific gravity at temperatures considerably above that of the laboratory it is convenient to use a Sprengel or Ostwald pyknometer. This is filled with the sample, suspended in water at the required temperature and adjusted, then removed, dried on the outside, cooled to room temperature and weighed. For a detailed description of the standardization of pyknometers at high temperatures consult any standard work on physico-chemical measurements or Bulletin 46 or 65, Bureau of Chemistry, U. S. Department of Agriculture.

Index of Refraction.

The index of refraction, like the specific gravity, increases with the proportion of unsaturated, or of hydroxy-acids. Unlike the specific gravity, the index of refraction increases with the molecular weight in the homologous series of saturated acids so that the presence of the fatty acids of low molecular weight in butter causes this fat to have a lower index of refraction than other animal fats, while its specific gravity is higher. In almost all of the fatty oils the index of refraction varies with the specific gravity so that in routine work it is not necessary to make both determinations but either may be used to confirm the inferences drawn from the other determinations.†

The index of refraction has usually been determined by means of the Abbe or the Pulfrich refractometer. The " oleo-refractome-

* McGill: *Analyst*, 1896, 21, 156.

† For a very full discussion of the relation of index of refraction to specific gravity in oils and fats see Proctor: *Journ. Soc. Chem. Ind.*, 1898, 17, 1021.

ter " of Amagat and Jean is a differential instrument in which the results are found in terms of an arbitrary scale, the value of which, according to Allen, is not constant. The readings of this instrument cannot, therefore, be compared with determinations of the true index of refraction. The " butyro-refractometer " of Zeiss also has an an arbitrary scale but in this case the values of the scale readings are known and can be compared with direct determinations of the index of refraction as follows:

Butyro-refractometer Reading.	Index of Refraction.	Butyro-refractometer Reading.	Index of Refraction.	Butyro-refractometer Reading.	Index of Refraction.
0	1.4220	40	1.4524	80	1.4783
10	1.4300	50	1.4593	90	1.4840
20	1.4377	60	1.4659	100	1.4895
30	1.4452	70	1.4723		

Since the butyro-refractometer is constructed to cover only such a range in the index of refraction as is likely to be met in work with fats and oils, it is possible to make more delicate readings with this instrument than with the Abbe refractometer. It is preferable, however, to express all results in terms of the index of refraction, especially as some substances frequently mixed with oils and fats are too highly refractive to be examined in the butyro-refractometer.

The index of refraction decreases with rising temperature. The rate of change is nearly constant for the common oils and fats, a rise of 1° causing a diminution of 0.000365 in the index of refraction.*

Directions for the determination of the index of refraction will be found in Kohlrausch's Physical Measurements, Leach's Food Inspection and Analysis, Lewkowitsch's Oils, Fats, and Waxes, or Vaubel's Quantitative Bestimmung organische Verbindungen.

Melting and Solidifying Points — Titer Test.

The melting point of a fat, or of the mixed fatty acids obtained from it, increases with the mean molecular weight among acids of the saturated series, while in mixtures of acids of the saturated and unsaturated series (or their glycerides) the melting point becomes lower as the proportion of unsaturated compounds increases.

* Proctor: *Journ. Soc. Chem. Ind.*, 1898, 17, 1023. Tolman and Munson: *Journ. Amer. Chem. Soc.*, 1902, 24, 754.

The melting point of a solid fat is best determined by heating a thin disc of the substance suspended in a mixture of water and alcohol as described in Chapter XI. This method being applicable only to substances practically insoluble in alcohol, the melting point of a mixture of fatty acids or of a wax may be taken as follows: *

Draw up the melted fatty acids (or the wax) into a very thin-walled capillary tube 3 to 5 cm. long according to the length of the bulb of the thermometer to be used. Seal one end of the tube and allow the substance to cool on ice for 12 to 15 hours. Attach to the bulb of a delicate thermometer graduated to 0.2°, immerse in water and heat very slowly. The temperature at which the substance becomes transparent is taken as the melting point.

The so-called "titer test" is the determination of the solidifying point of the mixed fatty acids. This test is largely used as a means of determining the suitability of fats for soapmaking and the details of manipulation are now being studied with a view to the adoption of a uniform method.† The Dalican process which has been quite commonly used is fully described by Lewkowitsch.

Viscosity.

The presence of glycerides of hydroxy-acids, whether natural as in castor oil or artificial as in the "blown" oils of commerce, gives a very high viscosity compared with fatty oils in which hydroxy-acids are absent. Among the latter, viscosities vary as a rule with the melting points of the mixed fatty acids. While the viscosity may aid in the identification of fats and oils in certain cases, its determination is especially important in the examination of lubricating oils and will therefore be discussed in that connection.

Heat of Combustion.

The heat of combustion of fats and fatty oils is a property as nearly constant as the specific gravity to which it stands in approximately inverse proportion, being lowered by the presence of acids of low molecular weight, highly unsaturated acids, or acids containing hydroxyl groups. The heats of combustion of butter-fat drying oils, castor oil and blown oils are therefore lower than

* U. S. Dept. Agriculture, Bur. Chem., Bul. 65.

† Tolman: Bul. 81, Bur. Chem., U. S. Dept. Agriculture.

those of body fats and such fatty oils as olive, almond, peanut or rape-seed. Waxes and hydrocarbons have higher heats of combustion than the glycerides. The same is true of the alcohols of very high molecular weight such as cholesterol and phytosterol of which the so-called unsaponifiable matter of fats is chiefly composed. With a suitable oxygen calorimeter the heat of combustion can be very accurately determined and the results are often useful in verifying the conclusions drawn from other determinations. For fuller discussions see the *Journal of the American Chemical Society*, 1896, 18, 178; 1901, 23, 164; 1902, 24, 348; 1903, 25, 659.

ALCOHOLS OF FATS AND WAXES.
(UNSAPONIFIABLE MATTER.)

Under the term "unsaponifiable matter" are included all substances found in fats and waxes which are insoluble in water and do not combine with caustic alkali to form soluble soaps. In a commercially pure fat or wax the "unsaponifiable matter" consists chiefly of one or more alcohols of high molecular weight, the more important of which are mentioned below.

The common waxes yield 50 to 55 per cent. of insoluble alcohols while the total amount of unsaponifiable matter in fats is much lower, being usually less than 1 per cent. in animal and less than 2 per cent. in vegetable fats.

ALCOHOLS OF THE SERIES $C_nH_{2n+2}O$.

Cetyl alcohol, $C_{16}H_{34}O$, occurs as palmitate in spermaceti. It is a tasteless and odorless solid, insoluble in water but soluble in alcohol and very easily soluble in ether or benzene. Melting point 50°; specific gravity at 99°, 0.7837.

Octodecyl alcohol, $C_{18}H_{38}O$, also occurs as ester in spermaceti. It is similar in properties to cetyl alcohol. Melting point 59°; specific gravity at 99°, 0.7849.

Myricyl alcohol, $C_{30}H_{62}O$, occurs as palmitate in beeswax and both free and combined in carnaüba wax. It melts at 85° to 88° and is nearly insoluble in cold, but readily soluble in hot, alcohol.

Other alcohols of this series are known but need not be considered here. From the examples given it will be seen that the melting points rise and the alcohols become less soluble with increasing molecular weight. The specific gravity, however, does not decrease as in the case of homologous fatty acids.

Cholesterol and Related Alcohols.

Cholesterol, $C_{26}H_{44}O$, is the characteristic constituent of the unsaponifiable matter of animal fats. It is only sparingly soluble in cold dilute alcohol or cold petroleum ether, but dissolves readily in ether, chloroform, carbon bisulphide, fatty oils, turpentine, or hot strong alcohol.

Phytosterol and *sitosterol* are alcohols, probably isomeric with cholesterol and resembling it closely in physical properties, which occur in vegetable fats, the latter being found especially in the oils of the cereal grains. The identification of one of these alcohols may therefore aid in determining the origin of an oil or fat or in the detection of vegetable fats present as adulterants in the more expensive fats of animal origin. The identification is best accomplished by converting the alcohol into an ester, the properties of the esters being more distinctive than those of the free alcohols. For further information regarding these alcohols see Lewkowitsch's *Oils, Fats, and Waxes* (3d ed.), pages 138–144 and the papers of Bömer,* Burian,† Ritter,‡ and Gill and Tufts.§

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* *Ztschr. Unters. Nahr.-Genussm.*, 1898, 1, 21, 81, 532; 1899, 2, 46, 705; 1901, 4, 865, 1070; 1902, 5, 1018.

† *Monatsh. Chem.*, 1897, 18, 551.

‡ *Ztschr. physiol. Chem.*, 1902, 34, 430, 461; 35, 550.

§ *Journ. Amer. Chem. Soc.*, 1903, 25, 251, 254.

TABLE OF ANALYTICAL PROPERTIES OF TYPICAL OILS, FATS, AND WAXES

Only those properties which are most frequently used in identification and testing for adulterants are included in this table. The numbers given are intended to indicate the normal range rather than the extreme limits. Results outside of these limits may be obtained upon pure samples but such discrepancies are usually due to abnormal quality or to changes resulting from manipulation or exposure. The figures are taken from the books listed at the end of the chapter, from bulletins and journal articles, and in a few cases from determinations not previously published.

Substance.	Saponification Number.	Iodine Number.	Specific Gravity at 15 to 15.5° / 15 to 15.5°	Specific Gravity at 99° / 15.5°	Index of Refraction at 60°.	Melting Point.	Source
Cocoanut oil.	246–268	8– 10	0.9245	0.863–0.874	1.438 –1.443	20°– 28°	Seeds of *Cocos nucifera.**
Butter fat.	220–236	26– 38	0.936–0.940	0.865–0.873	1.445 –1.449	28 – 35	Cow's milk.
Japan wax (tallow).	210–238	4– 15	0.960–1.010	0.8755	1.450 –1.452	45 – 56	Seed coverings of *Rhus succedanea.**
Palm oil.	196–206	50– 57	0.921–0.925	0.857–0.860	1.450 –1.452	27 – 43	Fruit of *Elacis guineensis.**
Cacao butter.	192–202	32– 42	0.945–0.980	0.858	1.449 –1.451	24 – 34	Seeds of *Theobroma cacao* (cocoa nibs).
Oleomargarine (oleo oil).	193–200	40– 55	0.925–0.930	0.858–0.863	1.452 –1.454	33 – 39	Pressed from beef tallow.
Beef tallow.	193–198	35– 45	0.925–0.929	0.860	1.449 –1.452	42 – 49	Body fat of cattle.
Mutton tallow.	192–196	32– 45		0.858–0.860	1.451	44 – 50	Body fat of sheep.
Lard.	193–198	50– 70	0.931–0.936	0.859–0.864	1.450 –1.454	36 – 46	Body fat of swine.
Cottonseed stearin.	193–196	88–104	0.919–0.923	0.864–0.869		26 – 40	Seeds of *Gossypium herbaceum.*
Spermaceti.	122–136	0– 5	0.905–0.960	0.808–0.816		42 – 49	Head and blubber of sperm whale.
Beeswax.	87–107	7– 11	0.959–0.975	0.818–0.827	1.447–1.449†	61 – 70	Honey combs.
Carnaüba wax.	78– 85	13.5	0.990–0.999	0.8422	1.462–1.465†	83 – 91	Leaves of *Corypha cerifera.*
Paraffin.‡	0		0.868–0.915	0.748–0.760	1.433–1.436†	52 – 55	Petroleum, ozokerite.
Rosin (colophony).	175–195	140–160	1.04 –1.11		1.548§	80 –100	Wood of several species of pine.

* Obtained also from other species of the same genus.

† Determined at 65° to 90°. Results are calculated to 60° for convenience of comparison.

‡ Such as is likely to be mixed with beeswax.

§ Temperature of observation not known.

Oil.	Saponification Number.	Iodine Number.	Specific Gravity at $\frac{15.5^{\circ}}{15.5^{\circ}}$.	Index of Refraction at 15.5°.	Specific Temperature Reaction.	Heat of Combustion Calories Per Gram.	Source—(German Name)—"Trade Name."
Linseed.	188–196	170–200	0.931–0.937	1.482 –1.485	270–350	9,375	Seeds of *Linum usitatissimum*—flax.
Tung.	190–197	150–170	0.934–0.942	1.5042	290–370		Seeds of Chinese and Japanese trees—"wood oil."
Hemp.	190–195	140–160	0.925–0.931	1.478 –1.480	230–285		Seeds of *Cannabis sativa* (Hanfoel).
Menhaden.	187–193	140–180	0.927–0.933	1.480	305–360	9,366	Bodies of menhaden often mixed with other fish.
Codliver.	175–190	135–180	0.922–0.933	1.479 –1.485	240–280	9,436	Livers of cod and dorsch.
Seal.	184–196	125–155	0.922–0.930	1.479 –1.483	210–260	9,424	Blubber of seals (Robbenthran, Seehundsthran).
Whale.	188–194	106–135	0.918–0.931	1.476	157	9,473	Blubber of whales (Walfischthran)—"train oil."
Poppy.	189–197	133–143	0.923–0.927	1.476 –1.478	200–240	9,382	Seeds of *Papaver somniferum* (Mohnoel).
Sunflower.	188–196	104–135	0.920–0.927	1.474 –1.478	167		Seeds of *Helianthus annuus.*
Maize.	188–194	111–124	0.921–0.926	1.4755–1.477	160–200	9,423	Seed germs of *Zea mays*—"corn oil."
Sesame.	187–195	102–115	0.920–0.925	1.474 –1.4765	140–175	9,395	Seeds of *Sesamum orientale.**
Cottonseed.	190–197	102–115	0.920–0.925	1.4735–1.476	140–175	9,396	*Gossypium herbaceum* (Baumwollsamenoel).
Mustard.	170–180	92–115	0.912–0.920	1.474 –1.4765	130–190		Fatty oil of black and white mustard seeds.
Rape (colza).	170–180	92–109	0.912–0.920	1.474 –1.476	125–155	9,476	Seeds of *Brassica campestris* (Rüboel).
Almond.	188–195	93–102	0.915–0.920	1.4725–1.475	95–120	9,454	Sweet and bitter almonds (Mandeloel).
Arachis.	186–196	85–105	0.915–0.921	1.471 –1.475	105–140	9,412	Peanuts, earthnuts—*Arachis hypogæa.*
Olive.	186–196	78– 90	0.915–0.918	1.470 –1.472	90–110	9,454	Fleshy fruit of *Olea europæa.*
Lard oil.	190–198	65– 82	0.915–0.918	1.469 –1.472	80–100	9,449	Pressed from lard.
Neatsfoot.	190–198	65– 75	0.914–0.918	1.468 –1.473	70–100		Feet of cattle.
Castor.	173–186	82– 90	0.960–0.970	1.479 –1.481	84– 94	8,849	Seeds of *Ricinus communis*—castor beans.
Sperm.	125–145	78– 90	0.875–0.885	1.465 –1.468	100	9,946	Head and blubber of sperm whale.
Rosin oil.	10– 35	40– 80	0.966–0.990	1.535 –1.550	72	10,145	Distilled from crude rosin.
Mineral oil.	0	0– 15	0.78 –0.92	1.434 –1.507	0– 20	10,700–11,200	Burning and lubricating oils from petroleum.

* Obtained also from other species of the same genus.

CHAPTER X.

Fatty Oils — Special Methods.

SALAD OILS.

Most salad oils are sold as olive oil. The principal substitutes and adulterants are cotton seed, arachis (peanut), sesame, rape, maize, poppyseed, and lard oils. Both quantitative and qualitative methods must be used in any thorough examination of an oil for adulterants. As a rule an oil should be pronounced adulterated only when quantitative determinations yield results which could not be obtained from a pure oil of normal character. Qualitative tests are usually required to show which of several possible adulterants is present. As yet certain color reactions are indispensable for this purpose, but in using these tests and interpreting the results it must be remembered that they depend upon the presence of constituents which may be removed or destroyed by improved methods of refining, and that olive oil which has been altered by long exposure to air in loosely stoppered or partially filled vessels, or oil containing a small amount of some accidental impurity, may give a reaction which cannot be distinguished from that of the adulterant sought. The results of even the best of the color reactions must therefore be interpreted with great caution and must usually be regarded as of much less significance than the quantitative numbers.

On the other hand a good grade of arachis oil, or a carefully prepared mixture of lard oil with one of the seed oils, can be added to olive oil in large proportion without affecting the ordinary constants to such an extent as to pass the limits which can fairly be regarded as normal. It is necessary, therefore, not only to compare each number found with the established limits for pure oil, but also to view the quantitative results in their relations to each other and to the indications of the qualitative tests.

While the system to be followed and the number of tests required will naturally vary in different laboratories the following may be recommended. Determine accurately the specific gravity, the iodine number, and saponification number. If an abundance of the sample is at hand determine the specific temperature reaction and the acidity. The index of refraction may be found, if

convenient, but is usually of less importance than the other determinations. Apply the nitric acid test, Halphen's test, one or more of the color reactions for sesame oil, and examine for arachidic acid by Renard's method. Finally, if the importance of the sample justifies the time required, separate and examine the unsaponifiable matter and the mixed fatty acids and determine the viscosity of the soap solution by Abraham's method described below.

Analytical Properties of Olive Oil.

The numbers included in the table of "constants" already given are intended to cover the range of normal variations in oils found in the American markets. Müntz, Durand and Milliau * examined samples from Africa, Spain, Portugal, Greece, Turkey, and the Levant without finding any significant variation in the specific gravity, iodine number, or temperature reaction. According to Milliau, Bertainchand and Malet, † however, Tunis oils have high specific gravities, the average of 49 samples being 0.9183. Tolman and Munson have recently examined a large number of olive oils many of which were of known origin. The following are taken from their results. ‡

Description.		Iodine Number.	Specific Gravity $\frac{15.5°}{15.5°}$.	Index of Refraction 15.5°.	Specific Temperature Reaction.	Free Acid as Oleic Per Cent.
California oils of known origin (42 samples).	Max.	89.8	0.9180	1.4718	109.7	8.21*
	Min.	78.5	0.9162	1.4703	94.5	0.20
	Avg.	85.3	0.9170	1.4713	101.8	1.20
Italian oils of known origin (17 samples).	Max.	86.1	0.9180	1.4713	104.7	2.79
	Min.	79.2	0.9155	1.4705	95.6	0.57
	Avg.	81.6	0.9163	1.4709	99.1	1.11
Italian oils (commercial) not found adulterated (57 samples).†	Max.	84.5	0.9179	1.4712	108.4	5.30
	Min.	77.5	0.9150	1.4701	88.4	0.72
	Avg.	80.9	0.9161	1.4706	97.8	2.42
French oils (commercial) not found adulterated (60 samples).	Max.	85.0	0.9183‡	1.4713	114.4	3.63
	Min.	79.0	0.9150	1.4699	90.4	0.45
	Avg.	81.3	0.9166	1.4708	100.1	1.59

* Two samples with larger amounts of free acid were found but were excluded from average as being unfit for use as salad oils.

† Omitting one sample containing 15.25 per cent. of free acid and having a specific gravity of 0.9134.

‡ Omitting one sample having an abnormally high specific gravity (0.9196) which may have been due to exposure.

* Bulletin du Ministère de l'Agriculture, 1895. Quoted from Bul. 77, Bur. Chem., U. S. Dept. Agriculture.

† Bulletin de l'Agriculture et Commerce de Tunis. Quoted from Bul. 77, *loc. cit.*

‡ Bul. 77, Bur. Chem., U. S. Dept. Agriculture.

The average iodine number of the oils from California is therefore higher than that of the French or Italian oils and, as might be expected, the higher iodine number is accompanied by a higher specific gravity, refractive index, and temperature reaction. Although individual samples will show slight variations, the same general relation is found on comparing oils which differ in iodine numbers though obtained from the same locality. Thus taking at random, from among the California oils of known origin examined by Tolman and Munson, 10 samples with high and 10 with low iodine numbers the following average figures were found:

	Iodine Number	Specific Gravity $\frac{15.5^{\circ}}{15.5^{\circ}}$	Index of Refraction 15.5°.	Specific Temperature Reaction.
First group.	88.44	0.9172	1.4716	105.7
Second group.	83.12	0.9166	1.4711	98.6

The normal relations of the constants to each other and the changes which may occur as the result of age or exposure * must always be taken into consideration when interpreting the results of an analysis.

Detection of Cottonseed Oil.

The presence of cottonseed oil in olive oil raises the specific gravity, iodine number, and temperature reaction and lowers the viscosity of the soap solution. A mixture of cottonseed and lard oils may, however, be added to olive oil in large quantity without greatly affecting any but the last of these "constants." The qualitative tests for cottonseed oil are therefore of considerable importance.

Halphen's Reaction.†

Dissolve 1 part of sulphur in 100 parts of carbon bisulphide and mix the solution with an equal volume of amyl alcohol.

Mix equal volumes, 2 to 3 c.c. each, of the reagent and the oil to be tested and heat the test tube containing the mixture gently at first until violent boiling ceases, then in a bath of boiling saturated solution of common salt. Heat for 2 hours unless a color develops sooner. If cottonseed oil is present the solution turns orange or red.

* See section on this subject beyond.

† Halphen: *Ann. Chim. Analyt.*, 1898, 3, 9; *Analyst*, 1898, 23, 131; Bul. 65. Bur. Chem., U. S. Dept. Agriculture.

This is probably the most sensitive and characteristic test for cottonseed oil and the least liable to give unsatisfactory results in the hands of an inexperienced person. The presence of 1 or 2 per cent. of unchanged cottonseed oil in olive oil is detected without difficulty. A reaction is often obtained * with lard or lard oil or even with butter fat † from animals which have been fed upon cottonseed meal. Copac (or kapok) oil, which is closely related to cottonseed oil, gives the same reaction. When heated at 250° for 10 to 20 minutes, cottonseed oil loses the property of giving this reaction. No pure olive oil has yet been known to give a similar coloration. Hence a positive result is considered conclusive but a negative result is not. The substance to which the reaction is due cannot be removed by treatment with animal charcoal ‡ and is supposed to be an unsaturated acid which combines with sulphur giving a red compound. §

Nitric Acid Test.

Cottonseed oil shaken at room temperature with an equal volume of nitric acid, of 1.37 to 1.38 specific gravity, gives a brown coloration, sometimes only on standing over night. Other seed oils give similar reactions. Normal olive oil under the same treatment shows no change of color.

The test is not so delicate as that of Halphen but is applicable to cottonseed oil which has been heated until it no longer colors the Halphen reagent. It may also be of value in determining whether a weak test with the latter reagent is due to a small amount of unheated cottonseed oil or to a larger amount which has been heated sufficiently to weaken the Halphen reaction (Tolman and Munson). According to Lewkowitsch this reaction cannot be relied upon to detect less than 10 to 20 per cent. of American cottonseed oil in olive oil. Tolman and Munson consider the test much more delicate. A positive result should always be confirmed by finding a high iodine number or by proving the presence of some other oil having a very low iodine number; for pure olive oil if much altered as the result of age and exposure will some

* Soltsein: *Ztschr. öffentl. Chem.*, 1901, 7, 140.

† Wauters: *Bull. Assoc. Belg. Chem.*, 13, 404; *Journ. Soc. Chem. Ind.*, 1900, 19, 172.

‡ Utz: *Chem. Rev. Fett. und Harz. Ind.*, 1902, 9, 125; Gill's Oil Analysis, p. 73.

§ Raikow: *Chim. Ztg.*, 1900, 24, 562, 583; 192, 26, 10. See also Halphen: *Bull. Soc. Chem.*, 1905, [3], 33, 108.

times give a reaction which cannot be distinguished from that of cottonseed oil.

Detection of Arachis (Peanut) Oil.

Arachis oil has usually a higher specific gravity and iodine number and practically always a higher temperature reaction than olive oil. The specific temperature reaction of arachis oil with concentrated sulphuric acid is usually 40 to 60 units higher than the iodine number of the same sample, whereas olive oil usually shows a difference of less than 20 and very rarely of more than 25 units between the iodine and the specific Maumené numbers. The presence of peanut oil in olive oil greatly diminishes the viscosity of the soap solution obtained on saponification. Any of these changes, however, might be due to other adulterants. Arachis oil is shown conclusively by isolating and identifying arachidic acid. This can be done with approximately quantitative results by Tolman's modification of Renard's method.

Renard-Tolman Test for Arachidic Acid. *

Weigh 20 grams of oil in an Erlenmeyer flask. Saponify with alcoholic potash, neutralize exactly with dilute acetic acid, using phenolphthalein as indicator, and wash the solution in a 500 c.c. flask containing a boiling mixture of 100 c.c. of water and 120 c.c. of a 20 per cent. lead acetate solution. Boil one minute and then cool by immersing the flask in water, occasionally giving it a whirling motion to cause the precipitated lead soaps to stick to the sides of the flask. After thorough cooling, pour off the water containing the excess of lead acetate and wash the soap with cold water and then with 90 per cent. alcohol. After pouring off the alcohol as completely as possible, add 200 c.c. of ether, cork the flask and allow to stand until the soap is disintegrated, then connect with a reflux condenser, heat gently to boiling and boil for 5 minutes on a safety water-bath or an electric heater. Cool to 15° and allow to stand over night.

Filter, wash the residue thoroughly with ether, and then transfer it from the filter to the flask by means of a stream of hot water acidified with hydrochloric acid. Add an excess of dilute hydrochloric acid and 200 c.c. of hot water and heat until the fatty acids

* Renard: *Compt. rend.*, 1871, 73, 1330.

Tolman: U. S. Dept. Agriculture, Bur. Chem., Bul. 81, p. 64. See also Archbutt: *Journ. Soc. Chem. Ind.*, 1898, 17, 1124.

separate as a clear oily layer. Nearly fill the flask with hot water and allow to stand at room temperature until the layer of fatty acids has completely separated and solidified. Remove and drain the cake of fatty acids, wash again with hot water, then dissolve in 100 c.c. of boiling alcohol, 90 per cent. by volume. Cool the solution to 15°, shaking frequently, and allow it to stand as long as any acid continues to crystallize out, or over night, at a temperature not above 20°. Filter, wash the crystals twice with 10 c.c. of 90 per cent. alcohol, noting the total volume of filtrate and washings, and then with alcohol, 70 per cent. by volume (in which the crystals are practically insoluble). Dissolve the crystals by means of hot absolute alcohol in a weighed dish, evaporate, dry, and weigh. To this weight add 0.0045 gram for each 10 c.c. of 90 per cent. alcohol in the filtrate and washings if the temperature of filtration was 20°; or 0.0025 gram for each 10 c.c. if the temperature was 15°.

The melting point of arachidic acid obtained in this way is 71° to 73°. According to Tolman and Munson * the determination of the melting point must not be neglected since cottonseed and lard oils have been found to give crystals resembling arachidic acid in appearance, but having a lower melting point. Tolman finds that from 5 to 10 per cent. of the oil can be detected by this method. On the usual assumption that the oil yields 5 per cent. of the acid,† each centigram found as described above (using 20 grams of oil) indicates 1 per cent. of arachis (peanut) oil in the sample.

Detection of Sesame Oil.

Sesame oil affects the usually determined constants in the same way as cottonseed oil and to practically the same extent. The color reactions are usually considered quite characteristic.

Boudouin's Test.

Dissolve 0.1 gram of sugar in 10 c.c. of hydrochloric acid of 1.18 to 1.20 specific gravity and add 20 c.c. of the oil. Shake thoroughly in a test tube for one minute and allow to stand. The water solution separates quickly and shows a distinct red or crimson color if the sample contains 1 per cent. or more of sesame

* U. S. Dept. Agriculture, Bur. Chem., Bul. 77, p. 35.

† This is probably more nearly a maximum than an average yield. Tolman and Munson (*loc. cit.*) obtained from 3.41 to 4.24 per cent.

oil. The active reagent is probably furfurol formed by the action of the acid upon the sugar.

Villivecchia's modification consists in shaking 10 c.c. of the oil with 10 c.c. of acid (1.20 sp. gr.) to which has been added 0.1 c.c. of a 2 per cent. solution of furfurol in 95 per cent. alcohol.

Olive oils of known purity have usually been found to give only a slight pink color, but sometimes the reddening of the water solution is so pronounced as to cause confusion with that produced by a small amount of sesame oil. Check experiments therefore should always be made. If much sesame oil is present the red color should be perceptible in the oily layer as well as in the water solution.

Tocher's Test.

Dissolve 1 gram of pyrogallol in 15 c.c. of concentrated hydrochloric acid. Shake this solution with 15 c.c. of oil in a separatory funnel and allow to stand for 1 or 2 minutes. Draw off the aqueous solution and boil for 5 minutes. The presence of sesame oil is indicated if the solution after boiling appears red by transmitted and blue by reflected light.

This test has not been so generally used nor so thoroughly studied as the preceding. The Association of Official Agricultural Chemists authorize the use of either Boudouin's, Villivecchia's, or Tocher's test for the detection of sesame oil in edible oils and fats.

DETECTION OF RAPESEED OIL.

The acrid taste of this oil would prevent the use of any but highly refined grades in salad oils and since, in America at least, refined rape oil is little if any cheaper than olive, it is not likely to be largely used as an adulterant. The presence in the oil of rape, and other seeds of the *Cruciferæ*, of large proportions of an acid (erucic) having a much higher molecular weight than oleic and linoleic, results in a low saponification figure and a high index of refraction together with low specific gravity. The determination of these constants would probably show rape oil in olive oil if 20 per cent. or more were present.

Rapeseed oil is less soluble than olive oil in acetic acid, but mixtures containing 20 to 40 per cent. of rape oil cannot be distinguished from olive oil by this test (Tolman).

Color reactions for rapeseed oil have been proposed but have not given satisfactory results.

Detection of Maize, Poppyseed and Lard Oils.

Each of these oils has a characteristic odor or taste, the odor of lard oil being intensified by heating. These properties, however, cannot be relied upon as the substances to which they are due can be almost entirely eliminated in the refining process. The effect of maize or poppy oil in raising the iodine number would be very noticeable but might be neutralized by the addition of a somewhat greater quantity of lard oil. The difference between the iodine number and the specific temperature reaction would be appreciably greater in such a mixture than in pure olive oil (compare detection of arachis oil). Maize and poppyseed oils react with nitric acid giving brown colors similar to that produced by cottonseed oil. Lard oil often gives the same reaction and might be indicated by the melting point of the fatty acids (those of lard oil having a relatively high melting point, 33° to 38° according to Tolman and Munson) or by the character of the unsaponifiable matter — phytosterol acetate test.*

All of these oils (as well as most others) yield soap solutions of much lower viscosity than those obtained from pure olive oils.† The determination and significance of this property has recently been studied in some detail ‡ and the method has been found capable of giving valuable results, especially if the conditions worked out by Abraham are carefully observed. For a full discussion of these conditions the original paper must be consulted. The essential features of the process are as follows:

Abraham's Modification of Blasdale's Viscosity Test.

The saponification number having been determined, weigh 3 grams of oil in an accurately graduated 100 c.c. flask, add 2 c.c. of alcohol and an amount of standard potash solution sufficient to saponify the oil and leave an excess of 0.625 gram of potassium hydroxide. Close the flask with a stopper having a Kroonig valve and saponify on a water-bath. After saponification expel the alcohol by warming and allowing air freed from carbon dioxide to pass through the flask, while a partial vacuum is maintained by means of a suction pump. In this way the alcohol is entirely removed in 5 to 10 minutes. Evaporation should not be carried to com-

*Bömer: *Ztschr. Unters. Nahr.-Genussm.*, 1901, 4, 1091.

† Blasdale: *Journ. Amer. Chem. Soc.*, 1895, 17, 937.

‡ Abraham: *Ibid.*, 1903, 25, 968. Sherman and Abraham: *Ibid.*, 1903, 25, 977.

plete dryness. Without allowing the flask to cool, add 50 c.c. of hot water, rotate gently until a homogeneous solution of the soap is obtained, cool to 20°, fill to the mark with distilled water and mix well by shaking or by repeatedly pouring the solution from one flask to another. Determine the viscosity of the solution in an Ostwald viscosimeter immersed in water kept at 20°. Care must be taken to avoid the introduction of air bubbles into the viscosimeter and to maintain the exact temperature. Repeat the readings until five or more concordant results are obtained. The viscosimeter is standardized by means of distilled water and it is advisable to select for this work an instrument in which the time of flow of water is about 100 seconds. Successive readings of a soap solution should then agree within 2 seconds.

The viscosity is calculated as follows:

$$v_1 = \left(\frac{s_1}{t}\right) t_1$$

where

v_1 = the viscosity number.
t_1 = the time of flow (in seconds).
s_1 = specific gravity of the solution.
t = time of flow of distilled water.

The viscosity numbers obtained by this method were:

Olive oil of known purity (9 samples)	168.0–185.7
Olive oil of doubtful purity (4 samples)	145.8–165.8
Lard oil (5 samples)	122.9–135.0
Arachis (peanut) oil (1 sample)	126.6
Cottonseed oil (3 samples)	126.6–127.9
Rapeseed oil "	124.7–125.7
Sesame oil (1 sample)	139.2
Maize oil "	126.6
Poppyseed oil "	123.9

Mixtures of olive and lard oils gave viscosity numbers agreeing closely with those obtained by calculation, but cottonseed or arachis oil when added to olive oil lowered the viscosity to a much greater extent than would have been predicted, indicating that the viscosity number is a more useful means of detecting adulteration than appears from a comparison of the results obtained on testing the olive oil and its adulterants separately.

The usefulness of the method for testing isolated samples is limited by the fact that comparable results can be obtained only

under strictly uniform conditions, the viscosity of the soap solution being greatly influenced by slight variations in strength, alkalinity, or temperature, while the terms in which the results are expressed will naturally vary with the form of viscosimeter used; but in cases of sufficient importance to justify the time required to arrange the apparatus and make comparative determinations, the "viscosity number" will be found an important factor in the examination of olive oil for adulterants.

DRYING OILS.

While other oils, including especially poppyseed and tung oils, are used as drying oils for special purposes, linseed oil is of much greater importance, being preferred in the great majority of cases in which a drying oil is needed. Only linseed oil and its adulterants will be considered here.

Analytical Properties of Linseed Oil.

Commercial linseed oil is usually designated by the region of its origin. It varies considerably, the variation being due mainly to the presence of foreign seeds in the linseed at the time of pressing. Hempseed is practically always present, sometimes in very small proportion but often to the extent of 5 per cent., or more, of the weight of seed. The drying properties of linseed oil are better the purer the seeds from which it is pressed. The iodine number and the drying power of the oil decrease as the proportion of hempseed increases. Hence a linseed oil containing much hemp oil would be shown to be of inferior quality by its low iodine number but could not be pronounced adulterated so long as this did not fall below 170. The maximum iodine number of linseed oil is difficult to fix since the results obtained by the method of Wijs often exceed the Hübl numbers, but since no other common oil has a higher iodine number than linseed, the maximum limit is of little practical importance in the detection of adulterations.

The usual range of the more important analytical constants of linseed oil has been given in the table at the end of the preceding chapter. The interpretation of "constants," their relations to each other, and their use in the detection of adulterations having been discussed in some detail in connection with the examination of salad oils, it will be sufficient in this case to mention briefly the principal adulterants with means for the detection of each, and describe the hexabromide test which distinguishes linseed from practically all other oils.

Adulterants and Methods of Detection.

Mineral Oil.

Mineral oil would greatly lower the iodine number, temperature reaction, and saponification number. Whenever a low saponification number is found the unsaponifiable matter should be separated and examined. Any mineral oil which is not volatile at 100° can be separated quantitatively, dried, and weighed. Volatile mineral oil can be distilled by means of a current of steam, separated from water in the distillate, and measured or weighed. In case turpentine were present, as in some so-called "boiled" oils, it would be distilled with steam and would separate from water in the distillate in the same way. The optical rotatory power of turpentine affords an easy means of distinguishing it from benzine or other volatile mineral oil.

Rosin and Rosin Oil.

Rosin dissolved in linseed oil raises the specific gravity and index of refraction while the saponification and iodine numbers are appreciably decreased only when large amounts of rosin are added. Presence of rosin greatly increases the acid number which in pure linseed oil is usually less than 7. Rosin acids can be separated and determined by Twitchell's method as described under soap analysis beyond.

Rosin oil in linseed oil would raise the specific gravity and greatly lower the saponification and iodine numbers. Rosin oil is a mixture of substances many of which are unsaponifiable, so that its presence in linseed oil would increase the amount of unsaponifiable matter.

Either rosin or rosin oil can be detected by the Liebermann-Storch color reaction or by determining the bromine substitution number.

Liebermann-Storch Reaction. — Shake 2 c.c. of the oil with 5 c.c. of acetic anhydride, warming gently. Allow to cool, draw off the anhydride and test by adding one drop of sulphuric acid (1 : 1). A violet color (not permanent) is produced in the presence of rosin or rosin oil. Cholesterol, which might be found in linseed oil if fish oil were present as an adulterant, gives a similar color reaction.

Bromine Substitution Number (McIlhiney). — Fatty oils take up bromine by direct addition, little or no substitution taking place. With rosin and rosin oil much the greater part of the bromine is

taken up by substitution, a molecule of hydrobromic acid being formed for each molecule of bromine which disappears. The hydrobromic acid thus affords a means of measuring the amount of substitution. It is determined by adding an excess of potassium iodate and titrating the liberated iodine. The same apparatus can be used as in the determination of the iodine number and the manipulation is similar. From 0.2 to 0.3 gram of the drying oil is dissolved in 10 c.c. of carbon tetrachloride and 20 c.c. of a one-third normal solution of bromine in carbon tetrachloride is added. After two minutes potassium iodide is added and the excess of halogen titrated by means of thiosulphate as in the determination of the iodine number. This shows the total amount of bromine which has disappeared. As soon as this titration is finished, add 5 c.c. of a 2 per cent. solution of potassium iodate and titrate the iodine set free from the iodate by the action of the free halogen acids, according to the reaction: $6HI + KIO_3 = 3I_2 + KI + 3H_2O$.

The bromine thus found is equal in amount to that which has combined with the sample by substitution. For further details of manipulation the reader must be referred to the original papers.* According to McIlhiney the bromine substitution number of raw or boiled linseed oil is always less than 7 while rosin oil gives numbers from 40 to 100 and rosin from 65 to 80.

Maize Oil.

The presence of maize oil in linseed oil lowers the specific gravity, index of refraction, iodine number, and temperature reaction. The amount which can be added without carrying these numbers below the normal limits of variation will depend upon the quality of the linseed oil in the mixture. Since the maize oil used as an adulterant of linseed would probably not be highly refined, the characteristic odor and taste would aid in its detection.

Cottonseed Oil.

The " constants " of linseed oil would be lowered by cottonseed in the same way as by maize oil and to a somewhat greater extent. If the cottonseed oil had not been heated, its presence would be detected by the Halphen test as described under salad oils.

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* McIlhiney: *Journ. Amer. Chem. Soc.*, 1894, 16, 275; 1899, 21, 1084; 1902, 24, 1109. See also Tolman: *Ibid.*, 1904, 26, 826.

Fish Oils.

Menhaden and other fish oils are often used as adulterants and are difficult to detect with certainty since their "constants" are frequently within the limits found for pure linseed oil. Their presence is often indicated by the odor, but this cannot be relied upon as the difference in odor between refined menhaden and low grade linseed oil is not so pronounced as might be supposed. Lewkowitsch recommends the determination of the melting point of the phytosteryl acetate obtained from the oil, and also that of the hexabromide of the fatty acids (see below). The crystals of phytoseryl acetate from pure linseed oil melt at 128°–129° (Bömer and Winter) while in the presence of cholesterol from fish oil much lower melting points are obtained.

Hexabromide Test.

Hehner and Mitchell* showed that linseed and fish oils differ from other oils in yielding considerable quantities of insoluble hexabrom-addition products when treated with bromine in ether solution. They applied the test directly to the oil as follows:

Dissolve 1 to 2 grams of oil in 40 c.c. of ether acidulated with glacialace tic acid, cool the solution to 5° and add bromine, drop by drop, until the solution is permanently colored brown. After standing for 3 hours, filter on asbestos and wash successively with 5 c.c. each of cold glacial acetic acid, alcohol, and ether. Dry the precipitate at 100° and weigh.

Linseed oil yields 23 to 38 per cent. of hexabromide, the amount increasing with the iodine number of the oil. Some of the fish oils yield equal or greater amounts, but tung, poppy, and walnut oils, and such seed oils as maize and cottonseed, yield almost no hexabromide, according to the figures compiled by Lewkowitsch never over 2 per cent.

Lewkowitsch recommends† that the test be applied to the mixed fatty acids rather than to the oil itself. In the separation of the acids care must be taken to avoid oxidation by exposure to air. The mixture of fatty acids from linseed oil yields 30 to 42 per cent. of hexabromide melting to a clear liquid at 175° to 180°, whereas the corresponding products from fish, liver, and blubber oils do not melt at this temperature but become darker and are completely

* *Analyst*, 1898, 23, 310.

† Oils, Fats, and Waxes (3d Ed.), p. 459.

blackened at about 200°. Lewkowitsch states that this test is capable of showing the presence of 10 per cent. of fish oil in linseed

OILS ALTERED BY AGE OR OXIDATION.

It has been assumed in discussing the analytical "constants" that the oils under examination are fresh or have been kept under such conditions as to prevent any material alteration. Age alone probably has no appreciable effect upon the analytical properties of commercially pure fatty oils, but such oils when kept for a long time in contact with air, for example, in partially filled or loosely stoppered vessels, take up atmospheric oxygen and gradually become considerably altered in those properties which are commonly regarded as "constants." This atmospheric oxidation naturally takes place much more rapidly with drying than with non-drying or semi-drying oils, and in open vessels than in those in which the oil is exposed to only a limited amount of air. It is probable that oils which have been thus altered are of much more frequent occurrence in commerce than has been supposed.

The influence of such oxidation upon the more important analytical properties is to increase the specific gravity, index of refraction, and temperature reaction with sulphuric acid, and to decrease the iodine number, the specific refractive power * and, in the case of olive oil, the viscosity of the soap solution. The acidity of the oil may increase at the same time but this change does not always occur.

The following results were obtained upon oils intentionally exposed to the air:

Oil.	Iodine Number.	Sp. Gr. $\frac{15.5°}{15.5°}$.	Index of Refraction at 15.5°.	Specific Refractive Power.	Specific Temperature Reaction.
Olive oil before exposure.	83.8	0.9165	1.4712	0.5141	100
Same after exposure.	77.3	0.9240	1 4722	0.5100	127*
Lard oil before exposure.	73.3	0.917	1.4697	0.5122	106
Same after exposure.	56.2	0.943	1.4724	0.5010	141
Cottonseed before exposure.	105.2	0.923	1.4737	0.5132	171
Same after exposure.	90.2	0.939	1.4779	0.5090	217*
Linseed before exposure.	177.1	0.934	1.4835	0.5177	
Same after exposure.	136.9	0.969	1.4886	0.5042	

*These numbers were determined earlier than the other results on the exposed samples and therefore do not show the full effect of the change.

*Calculated by Landolt's formula $\frac{N-1}{D}$, *i. e.*, $\frac{\text{Index of refraction} - 1}{\text{Specific gravity}}$. (*Ber. deut. chem. Ges.*, 1882, 15, 1031.)

Many other oils have been tested with similar results. It is evident that oils thus altered are very likely to be misjudged, especially if only one or two quantitative determinations are made. Thus if only the specific gravity and temperature reaction of the olive oil had been determined the results would have been interpreted as indicating the presence of some seed oil. The iodine number of the linseed oil taken alone would indicate extensive adulteration with some oil of lower drying power. The results emphasize the importance of determining the specific gravity and the iodine number in all cases and show the advantage of determining the temperature reaction not as a substitute for the iodine number but for comparison with it. For a fuller discussion of this subject with the results obtained upon a number of other oils the reader is referred to two papers in the *Journal of the American Chemical Society* (July, 1903, and May, 1905).

As the result of all of this work it appears that the increase in specific gravity and the decrease in iodine number are almost exactly proportional to each other in non-drying and semi-drying oils, so that in examining an altered oil belonging to either of these classes the original iodine number can be estimated by adding 0.8 to the number found on the exposed sample for each increase of 0.001 in the specific gravity. When the original specific gravity is not known the calculation must be based upon the average specific gravity for oil of the species under examination. The error in this assumption can hardly be sufficient to affect the interpretation of the results.

The iodine numbers of exposed samples of linseed and fish oils cannot be corrected accurately by the rule given for semi-drying and non-drying oils, the number thus obtained being always too low.

Commercial "blown" oils show greatly increased specific gravities and decreased iodine numbers; the changes appear to bear much the same relation to each other as in the oils which have been altered by exposure.

EXAMINATION OF AN UNKNOWN OIL.

In the examination of an unknown oil the specific gravity and the iodine and saponification numbers should be determined, and the appearance, odor, and taste compared with those of typical oils of known purity. The results thus obtained usually suffice to

locate the sample as one of a small group of oils, after which any special tests available for the detection of individual members of the group can be applied. The tests described in this chapter taken in connection with the quantitative determinations mentioned enable the analyst, in the majority of cases, to identify the oil or, if a mixture, the principal constituent.

If the saponification number indicates that only fatty oil is present, but the relation of the specific gravity to the iodine number does not correspond to that ordinarily found in any pure oil, the determination of the specific temperature reaction and the acidity will usually show whether the discrepancy is to be attributed to oxidation or adulteration.

The relative commercial value will of course determine what oils can profitably be used as adulterants. Prices vary greatly in different markets, as well as with the degree to which the oils are refined, and are also likely to fluctuate from year to year so that no fixed order of commercial value can be given.

The order of commercial value given by Gill and by Lewkowitsch show considerable variation, which doubtless is due largely to the differences between American and English markets. In each of the lists the highest priced oils are given first.

Gill. — Almond, castor, sesame, neatsfoot, rape, olive, sperm, whale, peanut (arachis), linseed, tallow, lard, fish, cottonseed, mineral, rosin oil.

Lewkowitsch. — Almond, sperm, olive, neatsfoot, lard, cod liver, arctic sperm, arachis, poppy, sesame, seal, rape, castor, cottonseed, maize, linseed, whale, fish, mineral, rosin oil.

In the examination of mixtures containing other than fatty oils, it may be necessary to separate the mixed fatty acids and examine this mixture in order to identify the fatty oils originally present. The "constants" of the fixed fatty acids of various oils, as well as of many oils and fats not mentioned in this work, are conveniently tabulated in Lewkowitsch's Laboratory Companion to the Fat and Oil Industries.

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THE NEW COURSE FOR CHEMICAL ENGINEERS AT COLUMBIA UNIVERSITY.

By Edmund H. Miller.

The training of technical chemists is a subject which has attracted the attention of both manufacturers and educators * for many years and judging by the numerous articles which have appeared and the diametrically opposite opinions which have been expressed, no apparent conclusion has been reached. In all probability it will be advantageous for this discussion to continue, as the curriculum of any institution is subject to improvement and alteration with changing commercial and educational conditions.

It is evident that there is a distinct demand for a kind of chemist which is not being produced; for a man who combines with a solid knowledge of chemistry considerable familiarity with both mechanical and electrical engineering, a man who is able to look at any proposition or process from the standpoint of the engineer as well as from that of the chemist; a man who can fill at first an analytical position but who is, on account of his engineering knowledge, better fitted to become a superintendent than the man trained only in chemistry, in fact a chemical engineer.

The demand for chemical engineers and the salient educational requirements have been given by Magnus Swenson in an article in the Bulletin of the University of Wisconsin, June, 1900, and recently in a paper by Mr. J. B. F. Herreshoff, which was read before the New York Section of the American Chemical Society on February 5, 1904, and discussed by Mr. Parker, of the General Chemical Company, Mr. Whittaker of the Welsbach Light Company, Dr. McMurtrie, of the Royal Baking Powder Company, Professor Hart, of Lafayette College, Dr. W. A. Noyes, of the Bureau of Standards, Professor Chandler, of Columbia University, Professor A. A. Noyes and Professor Talbot, of the Massachusetts Institute of Technology, Dr. Shieffelin, Dr. Schweitzer, Mr. Toch, Professor Bogert and Dr. Nichols, the president of the Society of Chemical Industry. This paper appeared with the discussion in *Science* for April 8, 1904, and should be read by those interested in this subject.

* W. A. Noyes, *Science*, March 7, 1902; Lachman, *Science*, May 16, 1902.

The present article deals with a definite plan for the education of chemical engineers, prepared after a careful consideration of the views of the chemists just mentioned. It has often been said and with truth, that it is impossible to make a man both a chemist and an engineer in four years, when it takes four years to make him either. It must be admitted at once that a much better chemical engineer can be turned out in seven years than in four. We need no new courses for this, the student graduates as an electrical or mechanical engineer and then, preferably after a couple of years of practical experience, returns to the university for the study of chemistry. Such a man has his engineering foundation, finds the need of chemistry by his factory experience, and brings to the study of chemistry a mature mind and an enlightened desire for knowledge. His work in chemistry should be emphatically a university course leading, after the courses in analytical, inorganic, organic, physical and industrial chemistry, to research work and finally to the doctor's degree. Such a man has had the best training for a technical chemist or chemical engineer for he has had both the engineering and the practical carrying out of work on one hand and the three years study of chemistry with research work to develop his ability for investigation, on the other.

There is, however, a powerful and practical objection to such a course — the expense. The problem to be met at present is to approach this ideal as nearly as is possible in a four years' course. Such courses have been established at the University of Pennsylvania, at the Massachusettes Institute of Technology and elsewhere. The course which follows differs from these in many respects, the most important being that it is based on higher entrance requirements, viz., sixteen points by the examinations of the College Entrance Examination Board in the following subjects, algebra, geometry and plane trigonometry, chemistry and physics with laboratory work, freehand drawing, English literature, composition and grammar, American and English history, French and German. No time is devoted to these subjects after admission, so that the entire four years is given up to chemistry, engineering, metallurgy, mathematics, mechanics, physics and mineralogy. It is only by starting with these high entrance requirements (for the details see the pamphlet of the College Entrance Examination Board) that enough time can be found for the subjects essential to the chemical engineer so the course to be given next fall at Columbia

University contains more chemistry and more engineering than any four years' course so far proposed.

In order to get the greatest benefit from such a course the student should be first, in good physical condition, and second, well prepared. The preparation can be obtained in some of the best high schools or better, he should have a couple of years of college training, so that the culture studies, particularly English, which are absent in the chemical engineering course, shall not be neglected.

The following is an outline of the four years' course in the School of Chemistry which has been established at Columbia University, the first year of which will go into effect in September, 1905. This course is based on the same entrance requirements as those in the School of Mines and School of Engineering and leads to the degree of Chemical Engineer.

First Year.

Mathematics.—Advanced algebra, spherical trigonometry and analytical geometry.

Physics. — Lectures and laboratory work on general physics, including electricity, sound, heat and light.

Chemistry. — Lectures and recitations on inorganic chemistry, recitations and practical work in qualitative analysis.

Mineralogy. — A short course including blowpipe analysis and the identification of the common minerals of economic importance.

Mechanical Drawing. — Use of instruments, elementary projections and descriptive geometry.

Shop Work. — Carpentry, wood turning, pattern making and foundry work.

Surveying. — Theory of surveying and five weeks' field work in the summer.

Second Year.

Mathematics. — Differential and integral calculus.

Mechanics. — Elementary, first half year; analytical, second half year.

Electrical Engineering. — General electrical principles and the elements of the dynamo.

Chemistry. — General industrial chemistry, including air, water, illumination, building materials, etc. Organic chemistry, lectures and six weeks' laboratory work during the summer session. Inorganic quantitative analysis, lectures, recitations and laboratory practice; chemical calculations.

Mechanical Drawing. — Machinery, furnace and structural work.

Mechanical Engineering. — Lectures on the steam engine.

Shop Work. — Threading, forging, welding, work at the lathe, milling machine, etc.

THIRD YEAR.

Mechanics. — Analytical mechanics first half year.

Electrical Engineering. — Lectures and laboratory work. Principles of electrical engineering, distribution of electric power, direct and alternating current machines.

Mechanical Engineering. — Lecture courses. Properties of materials. Mechanics of materials, the steam engine, the steam boiler. Laboratory courses in testing materials of engineering in experimental mechanical engineering. Also class and drafting room work in engineering design and graphical statics.

Chemistry. — Industrial chemistry, special course, lectures on the methods of manufacturing the principal inorganic acids, alkalies and salts. Lectures and laboratory work on organic and sanitary analysis and on assaying. Summer work in chemical factories.

Metallurgy. — Lectures on the metallurgy of copper and lead.

FOURTH YEAR.

Thermodynamics.

Hydraulics.

Mechanical Engineering. — Lectures on heat and its applications and practical work in machine design and in experimental engineering.

Work shop specifications and management.

Metallurgy. — Lectures on the metallurgy of iron and steel. Laboratory work on pyrometry, metallography, etc.

Industrial Chemistry. — Lectures on the organic industries including oils, fats, soaps, food, drink, textile fabrics, etc. Laboratory work in dyeing and in electrochemistry or in the preparation and purification of salts. Lectures and discussions of chemical factory apparatus and machinery and the cost of chemical operations in factories.

Physical Chemistry. — Lectures and laboratory work.

Thesis, with conferences and laboratory work.

The course requires sixteen to eighteen hours a week of lectures and recitations, laboratory work for three hours every afternoon

and five to six weeks' field, factory or laboratory work in the summer, so that in quantity of work it is equal to courses in mining and civil engineering as given at Columbia.

In the discussion of the training of a chemical engineer the opinion has been expressed that chemistry alone gives trouble enough to the ordinary mortal without engineering as well. This view is undoubtedly correct and is no criticism on the chemical engineering course; because there are already provided both in this country and abroad ample courses for the training of the scientific chemist; the man who is to fill positions in research laboratories and in colleges, who is to deal with chemical problems alone, who is to find out the facts and develop the theories which the chemical engineer will apply to commercial operations.

The object of the course described is not in any way to supplant the present training for men who mean to devote themselves exclusively to chemistry but to provide a kind of chemist, not now produced, for whom there is a demand by the chemical manufacturers of America.

THE COMPRESSION OF STOPE FILLINGS.*

By BERGASSESSOR JACOB OBERHAUSEN.

In the Ruhr coal district there is a generally accepted saying that when the rooms are filled with waste the amount of settling which takes place does not exceed 40 per cent. of the thickness of the seam; and that, as a rule, the settling is much less than this maximum. Up to the present time no definite data relating to the matter have been published. Certain small scale experiments, which were made at shaft No. 2 of the Kaiser mine by means of a brick machine, confirmed in a general way the supposition referred to above. The results of these experiments are given in Table I., which shows, for the various materials used for filling, an average compressibility of 32.3 per cent. of the volume originally occupied.

The exploitation at the above mentioned mine has recently furnished facts which lead to more definite conclusions as to the compressibility of the filling. These data being deemed of general interest are given below.

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* Translated by C. R. Corning and Robert Peele for SCHOOL OF MINES QUARTERLY, from Glueckauf, November 22, 1902, p. 1146.

TABLE I.

Character of Filling.	Weight per Liter, kgs.	Thickness of Filling.		Percentage of Compression, Referred to Original Thickness.	Remarks.
		Before Applying Pressure, m.m.	After Applying Pressure Three Times, m.m.		
White granulated slag.	0.550	74	39	47	The space in the press charged with filling was 255 m.m. long, 123 m.m. wide and 74 m.m. deep. The pressure die, weighing 700 kg., was dropped a distance of 142 m.m. Material to be tested had to be comminuted before charging the press.
Gray granulated slag.	0.722	74	42	43	
Dark gray granulated slag.	0.858	74	45	39	
Black granulated slag.	1.201	74	49	34	
Ground clay slate, up to 5 m.m. in size.	1.204	74	56	25	
Ground micaceous sandstone.	1.297	74	59	21	
Ground sandstone.	1.317	74	61	18	
Mason's sand.	1.250	74	53	28	
Cinder.	0.742	74	44	41	
Coal slack.	1.024	74	54	27	

The field of operations of the company lies chiefly in a district frequently flooded by the Rhine and the Ems. This induced the mine management to adopt the plan of filling the workings, in order to reduce to a minimum the surface depressions incidental to mining. In the area tributary to shaft 2, near Marxloh, this system has been carried out in a most complete manner. The daily production of 2,200 to 2,300 tons is won from rooms which are afterwards completely filled, together with the adjacent development work. The strata overlying the coal formation have an average thickness of 220 m. and consist largely of the younger formations, mainly Upper Cretaceous. The seams being mined are those marked No. 1 and *A*, *B*, *C*, *D*, and *G* on the accompanying section, and are at an average depth of 370 m. These seams vary in thickness between 1.8 and 0.5 m., averaging 1 m. The regular dip to the northwest usually does not exceed 25°, except in the western portion of the area, where, in the neighborhood of a fault, it reaches 60°. Its average is not over 15°. Between the individual seams the formation consists chiefly of clay-slates, sandstone, and sandy shales occurring only in three horizons, each 20 m. thick, situated respectively between seams *C* and *D*, *D* and *E*, *E* and *F* (Fig. 1).

The methods of mining employed, which depend on the nature of the seams and various local conditions, are as follows:

(*a*) Strebbau — long wall working, on strike or dip, either with straight face or series of stepped or off-setting faces.

(*b*) Stossbau — overhand breastwork, on the strike or to the rise, in horizontal slices, with use of filling.

(*c*) Stoss - Firstenbau — overhand breastwork, in steeply dipping seams.

The material which was used for filling comprises: (1) waste rock broken in mining the coal; (2) waste rock broken in prospecting and development; (3) waste picked out from the run of mine at the surface; (4) granulated slag from neighboring iron works.

For the normal production of 2,300 tons per 24 hours there are used as filling: of No. 1, 125 tons (250 loads); of No. 2, 250 tons; of No. 3, 15 to 20 tons, and of No. 4, 200 tons. This filling is conveyed to the working places partly through the air-ways and partly through the haulage gangways.

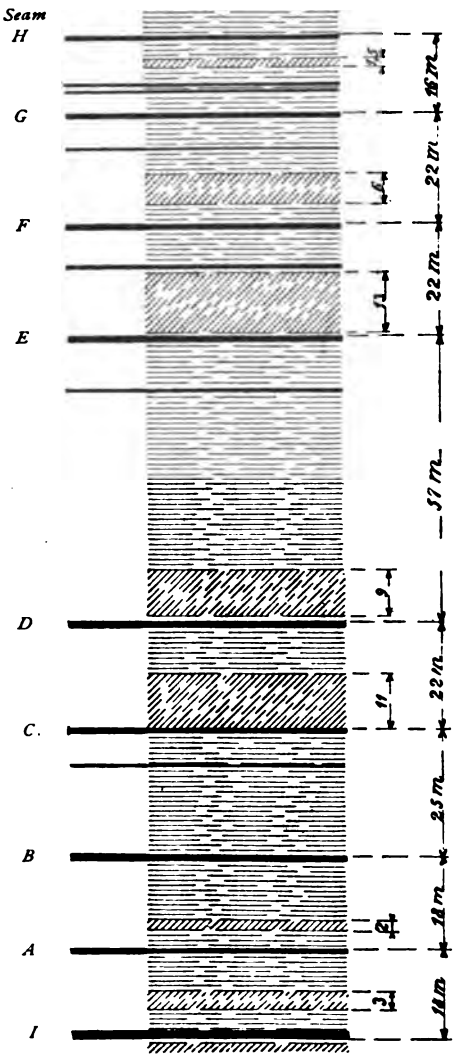


FIG. 1.

During the past year, at the Kaiser No. 2 mine, it has been decided that air and haulage ways which must be maintained for a long period of time are best run through the old stope fillings. For this reason several considerable portions of the mine, which were

worked out some years ago and subsequently filled, were again opened by drifting through them. The observations made in the course of this work are shown in the following table (p. 275):

The original thickness and composition of the seams was accurately known from former records, which have been carefully kept for each portion of the mine. The thicknesses of the worked out and filled seams were measured at a number of places during the driving of the new drifts, and the resulting averages are shown in the third and fourth columns of the table. By comparing the figures in these columns a coefficient is obtained showing the compressibility of the filling. This is given in column 5 as a percentage of the original thickness. Self-acting inclines, raises and air-ways were driven practically through the middle of the various worked out areas of ground detailed in columns 6, 7, 8, 9 and 10.

In columns 13 and 14 is noted the character of the country rock and of the filling as found in place where penetrated by the various new drifts. In all cases, excepting perhaps in seam *C*, it is quite evident that the settling within the seam itself had ceased. Between the foot and hanging walls the filling was hard and tight, having been even squeezed into fissures and cracks formed in the adjoining country rock. The filling forms a compact, breccia-like mass, and has been re-cemented, especially where granulated slag was used, into a hard material which could be broken only by blasting.

A comparison of the various data shows that in Stossbau and Strebbau (defined above), when granulated slag and broken rock were used for filling (seams 1, *D* and *G*) and when the drifts and inclines were filled at the same time, the settling was a minimum, averaging not over 26.5 per cent. of the original thickness. The settling was observed to be much greater when, instead of introducing outside rock, the filling was composed of country rock broken in the adjacent development work. Especially is this true when the drifts, self-acting, inclines, etc., were only partially filled (seams *A* and *B*). Under these conditions the settling amounted to 38 per cent. In seam *C* the rooms were only partially filled to a breadth of 6 m. with waste broken in the drifts. The adjoining drifts, which were two meters wide by 1.5 m. high, were originally left opon, and have not yet closed completely. Such material as they contain has in part been squeezed into them from the rooms. Here the settling has not ceased, although already amounting to something like 60 per cent. of the thickness of the seam, Fig. 2.

TABLE II.

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Designation of Coal Seam.	Dip of Seam.	Thickness. Before Stoping.	Thickness. After Stoping.	Per cent of Compression, referred to original thickness.	Size of Workings. Length on Strike.	Size of Workings. Length on Dip.	Size of Workings. Area Worked Out.	Average Depth from Surface.	Age of Workings at Time of Reopening.	System of Mining.*	Composition of Filling.	Character of Material through which new Gangways were Driven. Country Rock.	Character of Material through which new Gangways were Driven. Filling.
	Degs.	mm.	mm.		Met.	Met.	Sq. Met.	Met	Years.				
I	13	1,750	1,250	29	180	80	14,400	370	8	Stossbau; all drifts and inclines being filled with waste.	Waste rock: slates and sandstones from surface.	Hanging wall hard, foot-wall swelling ground.	Filling somewhat brecciated, completely compressed, very hard and had to be shot out.
I	16	1,790	1,290	28	260	80	20,800	450	2	Stossbau, as above.	Granulated slag and waste rock (clay slate) from development work.	Same as above.	Same as above, but still more brecciated in appearance.
A	15	1,070, including 290 mm. caved.	680	37	520	200	104,000	360	5	Strebbau; gangways and inclines only partially filled.	Waste from the seam, and from roof and foot-wall.	Hanging wall broken in large slabs; foot-wall hard and unaltered.	Same as No. 1.
B	10	1,355	820	39	440	60	26,400	300	4	Stossbau and Strebbau; same as A.	Same as A.	Hanging wall hard, foot-wall swelling ground.	Same as No. 1.
C	10	820	330	60	300	120	36,000	270	5	Strebbau; pillars 6 m. wide. Gangways and inclines 2 m. wide and remaining open.	Waste rock from bottom of gangways.	Hanging wall cracked but hard; foot-wall swelling ground.	Filling not entirely compressed; had flowed into portions of gangways. Could be broken by pick.
D	13	1,105	875	21	300	70	21,000	380	2	Strebbau; drifts and inclines being filled.	Waste rock from surface, with granulated slag and clay slate.	Same as C.	Same as No. 2.
G	36	1,075	780	28	320	80	25,600	440	2	Stossbau; filling same as in D.	Same as D.	Same as No. 1.	Same as No. 2.

* For definitions of systems of mining referred to in column 11, see p. 273. (TRANSLATORS.)

The facts noted in the table show that the compression will average 30 per cent. of the original thickness when the workings are completely filled with waste. Observations made in seam *C* indicate that with partial filling, that is, without introducing outside material to supplement the waste from the mining operations, and without filling the drifts and inclines, the amount of settling will still be materially less than that resulting from a system of mining with no filling whatever.

The results first mentioned in the preceding paragraph confirm in a measure the view generally accepted in the Ruhr district concerning the amount of settling which takes place when rock filling is employed; that is, when the filling is carefully and completely carried out, there need not be more than 30 per cent. settling. It is intended to continue these observations, and it is expected that the new system of filling now proposed at the Kaiser mine, in which granulated slag will be used, with water as a transporting agent, will show more favorable results than the old systems still in vogue.

SOME PRIMARY TRUSS PRINCIPLES.

By MYRON S. FALK, PH.D.

It is commonly supposed that all statically determinate structures are composed of an assemblage of triangles, this belief being based on the fundamental principle that the triangle is the only geometrical figure whose form may not be changed without varying the length of its sides.

Nevertheless, it may be shown that trusses, whose outlines contain rectangles, or even other polygonal figures, may be stable and statically determinate.

ART. 1. EQUILIBRIUM OF EXTERNAL FORCES ACTING ON TRUSSES.

The static equations of conditions necessary for the equilibrium of framed structures situated in one plane are but three in number; it is necessary, therefore, in the case of the unknown external forces acting on such a structure, that these be not more than three in number. Since the external loading is usually given, these equations furnish the conditions that the reactions may not include more than three unknown quantities.

A structure supported at two abutments has two reactions, and since a reaction is completely determined when its amount, direction and point of application are known, it follows that there are six unknown quantities in the general case of such a structure — three at each abutment. If each end of the structure is fastened to a frictionless hinge, the points of application of both of the reactions are fixed; there remain for that case but four unknown quantities. This is the case of a two-hinged arch, which is therefore not statically determinate. In that structure, however, the addition of a third hinge anywhere develops another equation of condition, viz., that the sum of the moments of all the external forces situated on one side of a section passed through this hinge must be zero about that hinge. For that structure there are then four equations of condition for four unknown quantities, and the reactions are statically determinate.

If, in the case of a two-hinged arch, one of the hinges be fastened to a nest of frictionless rollers so that the direction of the reaction through that hinge is made perpendicular to the direction of the path of travel of the rollers, then will only the amount of this one reaction be unknown and the reactions of the structure become statically determinate; for there are then three unknown quantities, to be found by the aid of three equations of condition.

This is the usual problem of a simply supported roof or bridge truss, in which case the structure has one fixed point of support, and one free end, resting on rollers. The fact that the reactions of such a structure may be determined by the static equations is however no criterion that the truss itself is either statically determinate or even stable; for those cases the truss itself must fulfill certain other conditions.

Art. 2. Equilibrium of Stresses in Members of Trusses.

For determining the equilibrium of each joint of the simple trusses described in the previous article, only two equations of condition can be applied; namely, that the sum of the horizontal and vertical components of the forces meeting at such joint are respectively equal to zero. For such concurrent forces the third equation of condition employing the moments of the stresses becomes inapplicable. Therefore, if k represents the number of joints in the structure, there will be $2k$ equations. If there are n members or bars in the structure, these $2k$ equations must be suffi-

cient to determine the stresses in the n members together with the values of the three unknown quantities in the reactions. Therefore, if all these unknown quantities are to be obtained by algebraic solution, and since the number of equations must equal the number of unknown quantities, the following equality must hold

$$2k = n + 3 \qquad (1)$$

or

$$n = 2k - 3. \qquad (2)$$

It is at once evident that if n is greater than $2k - 3$, the structure has redundant members; if n is less than $2k - 3$, the structure is in an unstable condition.

For a structure resting, then, on two or more points of support, the number of unknown quantities in the reactions may be represented by r. In order that these r quantities may be determined, it is necessary to have r equations of condition; of these r equations, three are already familiar, viz, $\Sigma H = 0$, $\Sigma V = 0$ and $\Sigma M = 0$. The other necessary equations as far as the static evaluation of the reactions is concerned, may be obtained by the insertion of $r-3$ hinges, each hinge furnishing an additional condition. The cantilever, with suspended spans, illustrates this form of structure, but it should be noted that not more than two hinges may appear between two neighboring points of support. The more general form of Eq. (2) applicable to any framed, coplanar structure is therefore

$$n = 2k - r \qquad (2a)$$

where r is the number of unknown quantities in the reactions. Eq. (2a) applies also to trusses supported at two points only, and in that case appears in the form of Eq. (2).

In general, therefore, a statically determinate truss must fulfill the conditions given in Eq. (2a); but if the structure does fulfill these conditions, Eq. (2a) is still no final criterion as to its stability. For the structure may be stable only under certain forms of loading, or the stresses in the members may be statically determinate, but infinite in magnitude even for relatively small loads. For instance, in the truss shown in Fig. 1, the number of members or n is 9, and the number of joints or k is 6. The conditions of Eq. (2) are fulfilled, since $2k = 9 + 3$; but inspection shows, at once, that the structure is not stable under all conditions of load.

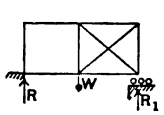


FIG. 1.

The final condition determining the stability of a structure requires, in addition to Eq. (2), that the determinant D, of the simultaneous equations expressing the equilibrium of the various joints of the structure, must not equal zero; the determinant may have a value greater or less than zero, but the solution of the equations becomes indeterminate if the determinant equals zero. The basis of this condition depends upon the theory of the solution of simultaneous equations, the treatment of which need not be here considered; the following general problem will however illustrate the methods to be employed.

Let $Z_1, Z_2, Z_3, \cdots, Z_{i=2k}$ represent the components of the unknown forces, and let

$$a_{1\cdot1} \quad a_{1\cdot2} \quad a_{1\cdot3}\cdots, a_{2\cdot1} \quad a_{2\cdot2} \quad a_{2\cdot3}\cdots, a_{i\cdot1} \quad a_{i\cdot2} \quad a_{i\cdot3}\cdots,$$

etc., and C_1, C_2, C_3, etc., represent known quantities, trigonometric functions and components of the loading respectively. Then the equations of condition will be represented in the most general form as follows, although in practice many of the constants will equal zero.

$$\begin{aligned}
a_{1\cdot1}Z_1 + a_{1\cdot2}Z_2 + a_{1\cdot3}Z_3 + \cdots a_{1\cdot i}Z_i &= C_1 \\
a_{2\cdot1}Z_1 + a_{2\cdot2}Z_2 + a_{2\cdot3}Z_3 + \cdots a_{2\cdot i}Z_i &= C_2 \\
\cdots\cdots\cdots

might however be evaluated, by the aid of the calculus, but its final evaluation even under those circumstances, would imply one of two conditions; either the stresses in some of the members become infinite for infinitely small applied loading, or the structure is stable only under particular forms of loading.

As is evident, the preceding treatment becomes involved when there are many members in the truss. A method to simplify the work, may however be employed.

Art. 3. Methods of Simplification.

A triangle is the simplest form of stable and statically determinate truss which can be imagined. According to the conditions noted in Eq. (2), this figure may be made more complex, although still remaining stable and statically determinate, if for every two additional members added to it one and only one more joint be added. Conversely, therefore, in a structure composed of many members, if it be possible to remove one joint simultaneously with every two members and the final resulting figure is a triangle, then the original structure must have been stable and statically determinate. If in removing these members and joints, the final figure is a frame work more complex than a triangle, but still capable of being shown to be stable and statically determinate, then the original structure must have been the same. In this latter way, then, the number of the simultaneous equations may be greatly reduced, and the value of the determinant may be more easily found.

Taking for example a simple Warren truss, such as shown in Fig. 2, its condition of static equilibrium is not rendered void by the addition of the members 1 and 2, nor by the members 3 and 4; but the members 2, 3, 4 and 9, inclose a rectangle. By the usual method of reasoning, this structure would at once be termed unstable. In this case, however, the structure is not only stable but statically determinate; although the members 3 and 4 receive no stress except under certain conditions of loading. In the same way, other members taken in the order of their numbering may be added.

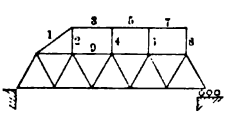


Fig. 2.

Application of Eq. (2) will show that this structure fulfills the required conditions there stated.

Fig. 3 shows this treatment applied to a truss which might be adopted in construction; its economy would doubtless not be very great. The numbering of the members shows the order in which they have been added.

Let there be considered the general problem of fastening together two statically determinate trusses such as shown in Fig. 4 by joining together one fixed and one free abutment point of each structure; let there then be determined the relations which must exist for static equilibrium when additional bars and joints are added to the resulting figure. Let ds represent the additional members; dk, the additional joints; s_1, the number of original members in truss No. 1; s_2, the number of original members in truss No. 2; k_1, the number of original joints in truss No. 1, and k_2, the number of original joints in truss No. 2. After the two trusses have been

FIG. 4.

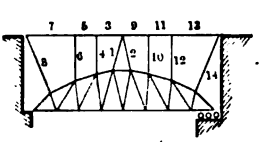


FIG. 3.

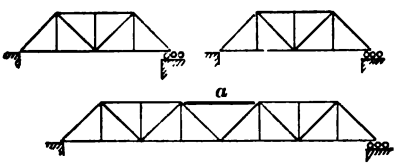


FIG. 5.

joined and new members and joints added, the total number of joints will be $k_1 + k_2 + dk - 1$, and the total number of members will be $s_1 + s_2 + ds$.

For static determination then,

$$s_1 + s_2 + ds = 2(k_1 + k_2 + dk - 1) - 3$$
$$= 2(k_1 + k_2) + 2dk - 5. \qquad (3)$$

But in the original figures

$$s_1 = 2k_1 - 3,$$
$$s_2 = 2k_2 - 3 \therefore ds = 2dk + 1. \qquad (4)$$

This last equality then signifies that the new members added to the resulting structure must always be greater by one, than twice the number of new joints. If there are to be no additional joints as in Fig. 5, which is adapted from Fig. 4, the combined structure must have added to it at least one new member before being stable; *i. e.*,

if $dk = 0$ then $ds = 1$,

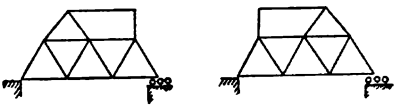
if $dk = 1$ then $ds = 3$, etc.

The additional member in this case is shown at *a*.

Let Fig. 6 represent two stable and statically determinate trusses, and let these be united into one structure by the preceding method; it will be seen that the final structure, Fig. 7, will be-

FIG. 6.

FIG. 8.



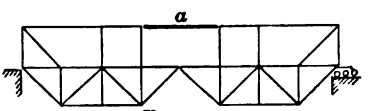


FIG. 7.

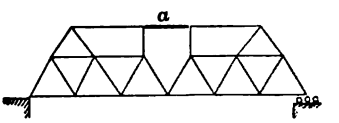


FIG. 9.

come statically determinate by the addition of the member *a* and it will be found to fulfill the conditions stated in Eq. 4. This truss, it will be seen encloses rectangles and at first inspection might be termed unstable.

Figures 8 and 9 represent another example; in this case, however, the final figure encloses a polygon of *five* sides; the member *a* is again the final member inserted to fulfill the conditions of Eq. 4.

In conclusion, it will be seen that none of the trusses developed offers any advantages over simpler types of structures; the purpose has merely been to show possibilities of design perhaps not generally known. For other interesting examples, the reader is referred to Müller-Beslau's "Die neueren Methoden der Festigkeits-lehre," to which the writer acknowledges his indebtedness.

MOLASSES AS FUEL.*

By R. TERRY, S. ARNOLD AND H. FISHER.

The subject of molasses as a fuel is one of considerable importance in all sugar-raising countries, and this thesis is an investigation of its efficiency when atomized in conjunction with fuel oil.

At present the oil output of the world is about 138,000,000 barrels per year. Russia producing 68,000,000, the United States 58,000,000, Dutch East Indies 3,000,000, Roumania 2,500,000, Austria Hungary 2,000,000. The remainder is subdivided among the other countries and is of little consequence from a commercial standpoint. The Russian oil differs greatly from that found in America. In the former the petroleum contains only 15 to 50 per cent. of kerosene, benzine, etc., and 50 to 80 per cent. of residuum, whereas in America product, 50 to 75 per cent. is kerosene, benzine, etc., and 25 to 50 per cent. residuum. This residuum, known variously as reduced oil tar, fuel oil, astatki, mazoot, petroleum refuse, etc., is what remains after the volatile constituents of the petroleum have been distilled off, and is the part of the oil used for fuel. Thus it will be seen that a much larger proportion of the Russian oil is adaptable for fuel than is the case in America.

The Pennsylvania Railroad uses 8,000 tons of coal per day, which is equivalent to about 26,000 barrels of oil or 9,500,000 barrels per year. This is one sixth of the total oil output of the United States, and considering that only 25 to 50 per cent. of the total output is available for fuel, the Pennsylvania Railroad alone would require close to one half of all the fuel oil; so that the lack of supply in this country prevents, for the present, its general use, besides which, our extensive coal fields render competition in price still more difficult.

The first serious application of oil to boilers was in the United States in 1861 to 62 by Shaw and Limston. A series of retorts was placed in the furnace, the oil entered at the top and in its descent parted with the more volatile elements while the residue was consumed in a corrugated receptacle at the bottom. From

* The investigation was carried out in the Mechanical Engineering Laboratories of Columbia University in the spring of 1905 as a graduating thesis under the direction of Dr. C. E. Lucke.

1863 to 1870 many experiments were carried on in England but the results claimed by some, and even by Admiral Selwin are extraordinary and often impossible. However, credit must be given for the successful construction of spraying devices, for they have served as models for many forms that have since given the best results. From 1883 to 1886 the French Admiralty conducted trials with marine and locomotive burners, using different atomizers with both air and steam; the former was satisfactory with pressures under 20 pounds. Heating the air was found to improve the evaporation one half pound; the amount of air used in spraying equaled 5 per cent. of the steam generated while 3.5 per cent. was sufficient when steam was employed; the highest evaporation was 15 pounds. In Russia Mr. Urquhart in 1884 was the first one to make a good reliable burner for locomotive practice, and since that time the spray device has been practically the only one employed commercially.

Molasses Composition and its Use.

Molasses is a viscid, usually dark colored uncrystallizable liquid which seeps from the massecuite of sugar cane or is thrown out by the centrifugal machines.

For every ton of cane ground an average of fifty pounds of molasses is produced and taking Hawaii's crop of 1903 as an example, reaching 3,500,000 tons of cane it follows that 87,500 tons of molasses resulted.

Molasses consists of about 25 per cent. of water and 75 per cent. of solid matter. It is proved beyond doubt from a scientific, as well as a practical standpoint, that if used in proper proportions with solid fuel, it furnishes a very valuable and cheap means to generate heat. Molasses as a fuel is nearly equal to bagasse. To create always a uniform heat the following method was used, considering the bagasse the cheapest material to be burnt with molasses. The proportions have been determined by the respective ratios of water and solid matter.

A sample of molasses has given the following analysis:

Total solids by evaporation	73.38
Sucrose D. P.	32.60
Glucose	29.96
Albuminoids	1.40
Other organic solids	4.32
Ash	6.10

There are several methods used in Java, Cuba, and Hawaii for burning molasses. The easiest way is to sprinkle the molasses on the bagasse as it leaves the last mill, on its way to the furnace, at the rate of about 50 lbs. molasses per ton of cane ground. Another way would be to atomize the molasses as fuel oil is atomized; either sprayed on an oil or coal fire, or with oil in the same burner.

Still another way, which by some is claimed to be the best, is the burning of the molasses in a retort furnace specially adapted to the purpose; an advantage of this method being that one-half the potash can be recovered and used as a fertilizer. Molasses could be used for the manufacture of alcohol, but the United States Internal Revenue tax now prohibits this use.

The calorific value of a sample of the molasses to be used for the boiler test was made by Dr. H. C. Sherman. The calorimeter was of Atwater Blakeslee Pattern.

The molasses was a sample of Canovanas Central Factory, Porto Rico, of the following composition, centrifugal:

Cane	20.40
Invert	34.48
Cane and Invert	54.88

TEST.

Weight of capsule and substance	3.8500
Weight of capsule	2.3088
Weight of substance	1.5412 grams.

Pressure of 22 lbs. of oxygen maintained in the calorimeter.

Readings taken for five minutes until constant or gradual variations were shown. Constant reading of 1.059, no current passing. Throwing on the electric circuit gave readings as follows:

Initial Period.		Corrected Readings.
1	1.059	1.065
2	1.059	
3	1.059	
4	1.059	
5	1.059	
$6\theta_0 =$	1.059	1.065
Main Period.		Corrected Readings.
$7\theta_1 =$	2.4	2.4
$\theta_2 =$	3.1	3.1
$\theta_3 =$	3.184	3.2
$\theta_4 =$	3.177	3.2
$\theta_5 =$	3.170	
$\frac{\theta_5 + \theta_0}{2} =$	2.1	

Final Period.

Sum = 14	Log. $V^1 - V$ = 7,782
$5\theta = 5.3$	Colog. $\theta^1 - \theta$ = 6,799
Difference = 8.7	3,976
Log. difference = 9395.	

Thermometer Correction.

T^0 of zero 16.

Correction for 1 degree	6.4
Rise (degrees)	2.1
	64
	128
Thermometer correction	13.44

Final Calculations.

$\theta_5 = 3.173$

$\theta_0 = 1.065$

$\theta_5 - \theta_0 = 2.108$

Thermometer correction	13.4
Rad. correction	25.0
Corr. rise	21,464
Corr. rise × 21 = total heat	42,928 / 4,507.44
Accessories	33.3
Corrected heat	4,474
Log. corr. heat	6,507
Log W.	1,879
	4,628

Heat of Combustion per gram = 2,903.

$\frac{2,903}{5} = 580.6$ Calories per gram.

$580.6 \times 9 = 5,225.5$ B. T. U. per pound.

Now, if we take an average analysis of Pennsylvania bituminous coal as 14,200 B. T. U. calorimetric test, we have for comparison with molases,

$\frac{5,225.4}{14,200} = 368$ lbs. of coal is equal to 1 lb. of molasses, which corresponds closely with Dr. Atwater's result of 376.

The same molasses was submitted to physical tests to determine the flash point, burning point and the peculiarities under heating. The apparatus consisted of a copper vessel containing sand, in which was partially buried a smaller vessel containing molasses. A Bunsen burner supplied the heat. At 150° F. the molasses began to bubble, forming a light yellow scum on the surface. As the temperature increased the liquid became less dense, the bubbling and the amount of scum became greater. At 182° F. a flame approached to the bubbles, appeared to burn with a blue

flame as the bubbles burst, though in the future tests this result could not again be obtained; also it was difficult to determine if the bubbles contained an inflammable gas or not, as the heat of the pilot flame may have produced the flash. At 216° F. the bubbles increased very rapidly. The blue flame did not appear on the bursting of the bubbles from 216°–224°, probably on account of the water becoming evaporated. At 240° all of the molasses had become bubbles, no liquid remaining. The thermometer was then removed and the heating continued. Bubbles continued to form and burst, and the color gradually deepened to a dark brown, whereupon gases were given off which burnt with a blue flame. This continued until nothing remained but a very hard and cakey black residue. This glowed in the bunsen flame for some time and was of a carboniferous nature, leaving finally a white ash.

On repeating the above a blue flame was obtained at 210° F. A whitish smoke in a more pronounced degree was given off at 250° F., becoming quite thick at 300° F.; it did not burn, but puffed out the pilot light. At 322° F. it began to flash. At 324° F. a continuous stream of combustible gas was given off, burning with a blue flame like hydrogen. To determine ash molasses was put in a crucible and the crucible was put in a reducing furnace and residue called ash.

CRUCIBLE TEST NO. 1.

Weight of crucible	101.37	grams.
" with molasses	106.55	"
" with coke residue	106.23	"
" with coke	4.86	"

CRUCIBLE TEST NO. 2.

Weight of crucible	109.23	grams.
" of crucible with coke	114.45	"
" of coke	5.22	"
" of crucible and ash	109.55	"
" of ash	.32	"
Per cent. ash in coke	6.13	

CRUCIBLE TEST NO. 3.

Weight of crucible	101.48	grams.
" of crucible with molasses	127.82	"
" of molasses	26.34	"
" of crucible with coke	110.15	"
" of coke	8.67	"
" of crucible with remaining coke	110.14	"

"	of coke	8.66	"
"	of crucible with ash	102.16	"
"	of ash	.68	"
Per cent. of coke in molasses		32.9	
"	of ash in coke	7.8	
"	of ash in molasses	2.58	

Other similar tests conducted in the same manner gave the following results.

TABLE I.

CRUCIBLE TEST.

No. of Test.	Per Cent. of Coke in Molasses.	Per Cent. of Ash in Coke.	Per Cent. of Ash in Molasses.
1	32	—	—
2	—	6.13	—
3	32.9	7.8	2.58
4	32.4	6.10	2.48
5	32	6.19	2.49

EVAPORATIVE TEST.

Description of Apparatus.

The evaporative value of the molasses as a fuel in a boiler was made in the locomotive in the laboratory. The method of weighing the injector water is shown in Fig. 1. The water is weighed in small barrel, *B*, and this in turn is emptied into hogshead, *D*, from

FIG. 1.

which it is injected into the locomotive. In the first test the oil was raised to the burner by air pressure. In the subsequent tests the arrangement of the oil barrels is shown in Fig. 1 by the letters *A*, *A*; the oil being supplied by gravity. In both cases the oil barrels were placed on scales, used alternately and weighed. The molasses was supplied by a duplex pump from a barrel placed on scales. The pump was a Worthington, size 2 × 1 ⅛ × 2¾ and was not able to lift the molasses from the barrel.

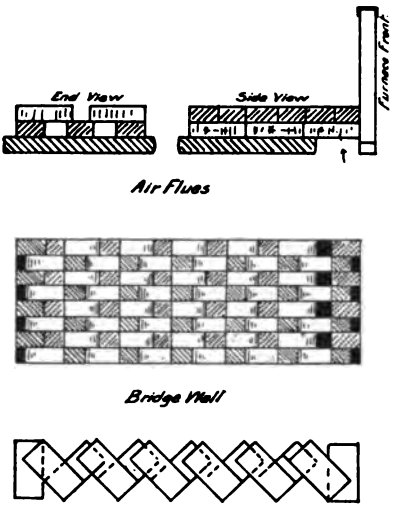


FIG. 2.

The grate bars were covered with fire bricks, and the interstices filled with fire clay. The bricks were removed as required in the various tests, to admit air for combustion. A fire brick wall as shown in Fig. 2 placed 5½ feet from the fire door. No arch was required, the burner being slanted downward. Both dampers were left open, and the steam jet in the stack was used to create a draft.

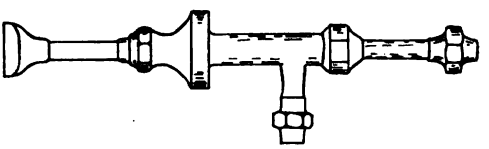
DIMENSIONS OF LOCOMOTIVE.

COLUMBIA.

Cylinders	High pressure	13″ x 26″
	Low pressure	22″ x 26″
Piston rod diameter		3½″
Steam ports		24″ x 1.5″
Sectional area of steam pipe opening connected with cylinder		19.63″
Drivers diameter		84″
Boiler straight		
Minimum internal diameter of boiler		54.75″
Number of tubes		198
Outside diameter of tube		2″
Distance between centers of tubes		2⅝″
Length of tubes over tube sheets		13′ 1¼″
Thickness of boiler plates—steel		⅝″
Length of fire-box inside		84 13/16″
Width of fire-box inside		42⅜″
Grate area		24.8 sq. ft.

Fire-box heating surface	128.23	"
Heating surface of tubes	1,349.9	"
Total heating surface	1,478.13	"
Width of grate bars		0.75″
Space between grate bars		

The burner of the National Oil Burner and Equipment Company, for atomizing oil, Fig. 3, was used first. The front nozzle



The National Oil Burner
FIG. 3.

of these burners was threaded with standard pipe thread, so that a pipe extension can be used where the lining of the furnace is unusually thick, as in open-hearth furnace. The piping for this burner is shown in Fig. 4 and Fig. 5, with connections for oil molasses and steam jacket heater.

APRIL 10, 1904. NATIONAL OIL BURNER AND EQUIPMENT COMPANY. FUEL—OIL.

Time of run	1 hr. 22 min.
Feed water	2,915 lbs.
Weight of oil	219 lbs.
Temperature of oil	130° F.
" of feed water	60° F.
Pressure on steam	85 lbs.
" on oil (burner)	12 "
" on air "	45 "
" on steam "	75 "
Calorimeter temperature	213° F.
" pressure	2⅝″ of water.
Lbs. of water evaporated per lb. of oil	13.3 lbs.
Factor of evaporation	1.194
Equivalent evaporation (from and at 212° F.)	15.88 lbs.

Part of the run was made using air and part using steam as an atomizing agent. The air for combustion was solely supplied through the burner and openings in the fire door. The grate bars were covered with fire bricks and cemented. The bridge was constructed as shown in Fig. 2. Perfect combustion was easily maintained.

The burner is designed for using the oil at not less than 40 pounds pressure. The prevalent American locomotive practice is to supply the oil to the burner by gravity, under which condition this burner could not supply enough oil for a locomotive boiler.

FIG. 4.

High evaporation efficiency was obtained for the oil burnt, but it was impossible to make steam fast enough to supply the cylinders. However, it shows fine results for stationary practice or marine boilers.

The Sheedy Garrick is one of the most widely used burners in railroad practice in the states. The Southern Pacific locomotives are equipped with them. The construction is shown in Fig. 6. The burner is made of bronze casting and of flat type design. It

consists of an upper oil, a central steam, and a lower air chamber. The oil enters the upper compartment through a 1 ¼-inch opening, and meets the steam jet just before reaching the mouth of the burner. Air is entrained in the lower chamber by the steam jet

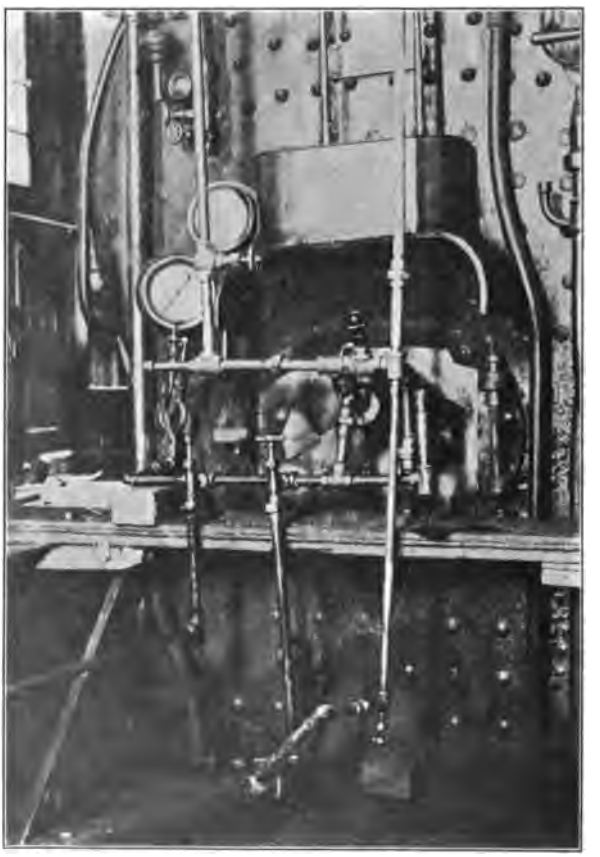


FIG. 5.

entering through a 1 ¼-inch opening at the bottom of the burner. This burner was piped as shown in Fig. 7.

The oil is atomized just before leaving the mouth of the burner. The only disadvantrge being that it gives the fireman one more thing to adjust, which is the air.

A comparative test of a Witt and a Sheedy Garrick burner performed on the Los Angeles division upon an engine with Vander-

bilt corrugated fire-box, gave for the former 11.86 pounds of water, evaporated from and at 212° F. per pound of fuel, and for the latter 14.10 pounds.

MAY 19, 1904. SHEEDY GARRICK OIL BURNER. FUEL—OIL.

Time of run	3 hours.
Feed water	11,225 lbs.
Weight of oil	1,001.5 "
Temperature of oil	140° F.
" of feed water	66° F.
Pressure of steam	100 lbs.
" of oil (burner)	Head.
" of air (burner)	4.5 lbs.
" of steam (burner)	7.5 "
Calorimeter temperature	213° F.
" pressure	2½° F. water.
Pounds of water evaporated per pound of oil	11.2 lbs.
Factor evaporation	1.193
Equivalent evaporation (from and at 212° F.)	13.36 lbs.

The oil heater was increased to twice the former size. This consisted in steam jacketing the oil pipe for 6½ feet. In this and

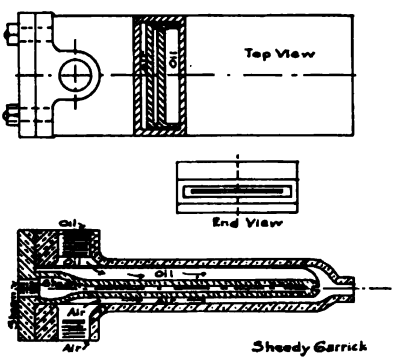


FIG. 6.

in the following test the oil is fed by gravity through a one-inch pipe.

MAY 19, 1904. SHEEDY GARRICK OIL BURNER. FUEL, MOLASSES AND OIL.

Time of run	1 hr., 17 min.
Feed water	4,446 lbs.
Weight of oil	389 lbs.
" of molasses	78.5 "
Temperature of oil	134° F.
Temperature of feed water	66° F.

Pressure of steam	100 lbs.
" of oil (burner)	Head.
" of steam (burner)	4 lbs.
" of air (burner)	2 lbs.
Calorimeter temperature	212° F.
" pressure	2½° F. water.
Pounds of water per pound of oil	11.2 lbs.
" " " " " molasses	1.16 "
Equivalent evaporation for oil (from and at 212° F.)	13.36 "
Factor evaporation	1.193
Equivalent evaporation for molasses (from and at 212° F.)	1.38 lbs.

FIG. 7.

This test was begun with the bricks in the furnace of the fire-box red hot. The molasses was sprayed in cold, was entirely consumed, not caking at all on the fire bricks and leaving a slight ash.

An inconsiderable deposit of soot remained on the walls of the fire-box.

MAY 27, 1904. SHEEDY GARRICK BURNER. FUEL—OIL.

Time of run	3 hrs., 5 min.
Feed water	9,157 lbs.
Weight of oil	964.5 "
Temperature of feed water	68° F.
" of oil	150° F.
Pressure of air (burner)	4.5 lbs.
" of steam "	11 "
" of oil	Head.
Steam Pressure	96 lbs.
Calorimeter temperature	212° F.
" pressure	3″ of water.
Lbs. of water evaporated per lb. of oil	9.5 lbs.
Factor of evaporation	1.193.
Equivalent evaporation (from and at 212° F.)	11.35 lbs.

MAY 27, 1904. SHEEDY GARRICK BURNER. FUEL—MOLASSES AND OIL.

Time of run	50 min.
Feed water	3,225 lbs.
Weight of oil	324 "
" of molasses	89 "
Temperature of oil	144° F.
" of molasses	140° F.
" of feed water	68° F.
Pressure of oil	Head.
Steam pressure	100 lbs.
Lbs. of water evaporated per lb. of oil	9.5 "
Equivalent evaporation for oil (from and at 212° F.)	11.35 "
Lbs. of water evaporated per lb. of molasses	1.41 "
Equivalent evaporation for molasses (from and at 212° F.)	1,682 "

In this and the following tests a 30″ steam jacket was put on the molasses pipe. The molasses atomized much better preheated than cold. In the latter case it left the burner in visible globules often falling down in front of the burner, whereas when preheated it left the burner in a fine spray and no dripping occurred.

JUNE 1, 1904. SHEEDY GARRICK BURNER. FUEL—OIL.

Time of run	1 hr., 50 min.
Feed water	6,030 lbs.
Weight of oil	645 "
Temperature of feed water	73° F.
" of oil	130° F.
Pressure of steam	110 lbs.
" of oil	Head.

Pressure of steam (burner)	12 lbs.
" of air "	4 "
Calorimeter temperature	213.5° F.
" pressure	2⅝" water.
Factor evaporation	1.185.
Lbs. of water evaporated per lb. of oil	8.99 lbs.
Equivalent evaporation (from and at 212° F.)	10.84 "

JUNE 13, 1904. SHEEDY GARRICK BURNER. FUEL—MOLASSES AND OIL.

Time of run	3 hours.
Feed water	10,000 lbs.
Weight of oil	1,094 "
Temperature of feed water	73° F.
" of oil	140° F.
" of molasses	130° F.
Pressure of steam	108° F.
" of oil	Head.
" of air (burner)	4 lbs.
" of steam (burner)	12 "
" of molasses (burner)	1.25 "
Calorimeter temperature	214° F.
" pressure	3" water.
Lbs. of water evaporated per lb. of oil (omitting molasses)	9.14 lbs.
Factor of evaporation	1.188
Equivalent evaporation (from and at 212° F.)	10.87 lbs.

JUNE 21, 1904. SHEEDY GARRICK BURNER. FUEL—OIL.

Time of run	2 hours.
Feed water	5,200 lbs.
Weight of oil	664 "
Temperature of feed water	73° F.
" of oil	142° F.
Pressure of steam	110 lbs.
" of air (burner)	4 "
" steam "	8 "
Calorimeter temperature	213.5° F.
" pressure	3" water.
Lbs. of water evaporated per lb. of oil	7.83 lbs.
Factor of evaporation	1.193
Equivalent evaporation (from and at 212° F.)	9.317

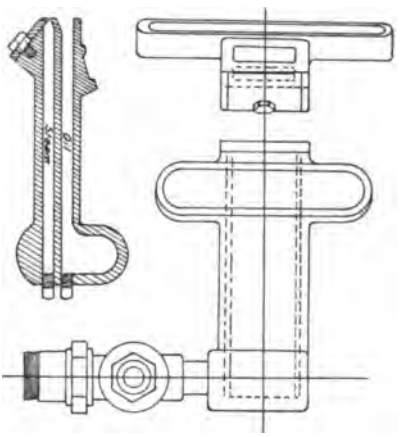
JUNE 21, 1904. SHEEDY GARRICK BURNER. FUEL—MOLASSES.

Time of run	1 hr., 35 min.
Feed water	4,800 lbs.
Weight of oil	570 "
" of molasses	271.5 "
Temperature of feed water	73° F.
" of oil	150° F.
Pressure of steam	100 lbs.
" of air (burner)	2 "

" of steam "	19 "
Calorimeter temperature	213.5° F.
" pressure	3″ water.
Pounds of water evaporated per pound of molasses	1.24 lbs.
Factor evaporation	1.188
Equivalent evaporation (from and at 212° F.)	1.47 lbs.

The above mixture was found to be the limiting practical ratio of molasses to oil. Any attempt to increase the former resulted in the formation of a coky mass in the center of the fire-box which augmented faster than it could burn. When, however, the molasses was shut off for a short time, this mass entirely disappeared, burning like coke and leaving a fine white ash.

In the system of the Baldwin Company steam is admitted to the lower part of the burner through a pipe so connected to the boiler as at all times to insure the introduction of dry steam. The valve controlling the steam is placed in the cab, close to the fireman's seat. A free outlet is allowed for the oil at the nose of the burner; the steam outlet, however, is contracted at this point by an adjustable plate which partially closes the port, and gives a thin wide aperture for the exit of the steam. This arrangement withdraws the steam and increases its velocity at the point of contact with the oil, giving a better atomizing effect. A permanent adjustment of the plate can be made for each burner after the requirements of service are ascertained. The moving of the plate is not, then, required except for cleaning purposes. The oil, as it passes through the burner, is heated to a certain extent by the effect of the steam in the lower portion, and flows freely in a thin layer over the orifice. It is here caught by the jet of steam issuing from the lower port, and is completely broken up and atomized at the point of ignition. The oil is carried into the fire-box in the form of vapor where it is thoroughly mixed up with air and burns freely.



The Baldwin Burner

FIG. 8.

It is computed that one inch of breadth of slit will serve for 100 square inches of cylinder area, so that the breadth of a burner is $B = D^2 \times .007854$. As only one burner is used, American fire-

Fire-box Baldwin Locomotive

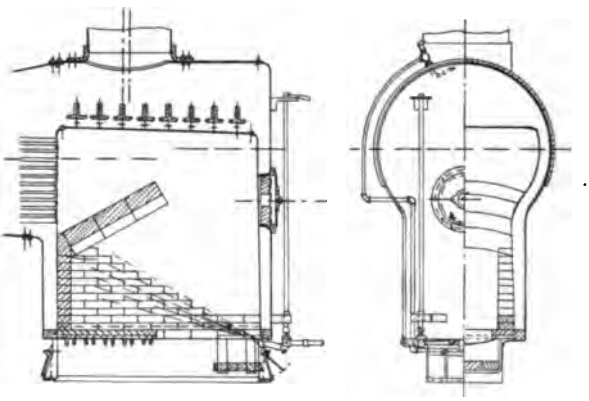
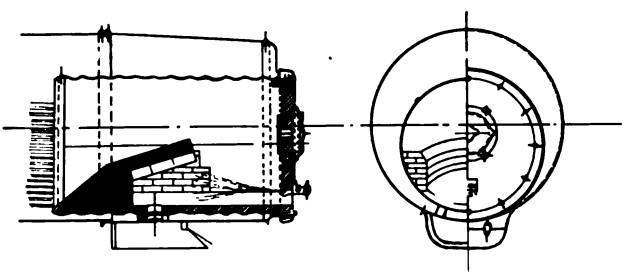


FIG. 9.

boxes being narrow, it is apparently the case that one cylinder is intended to be taken, and not the area of both cylinders. D = diameter of cylinder.

Large oil pipes are used so as to deliver a full supply as far as the regulating cock. To permit of fine adjustment of the cock its



VANDERBILT FIRE-BOX

FIG. 10.

orifice is not circular but square, with the diagonals vertical. The construction is shown in Fig. 8.

The atomizer is attached below the mud ring, and the spray is directed upwards into the fire-box, which is fitted with a brick arch, a liner of fire bricks and a base filling the front half of where

the grate usually is placed. A small hearth is also placed to catch any drip from the burner, and from the lower corner of the bridge there is built, to protect each side sheet, a triangular wall of bricks extending with its lower point to the back plate. The side walls form the sides of the fire brick combustion chamber. The "ash pan" is retained with its dampers, to admit air below

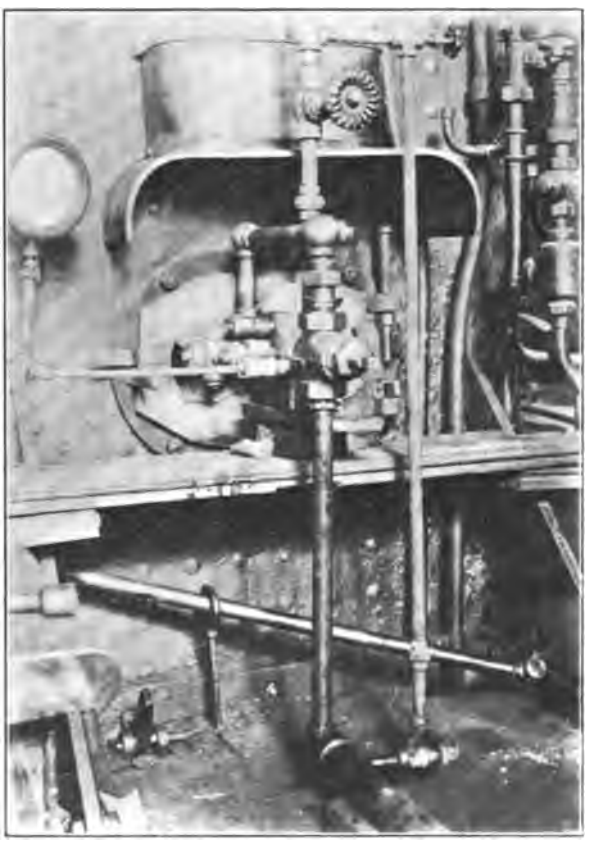


FIG. 11.

the fires, and the dampers should shut tight. Fig. 9 shows this arrangement.

The details of application to a Vanderbilt fire box are shown in Fig. 10. As used for these tests the piping and baffles were similar to those of previous tests and are given in Figs. 11 and 12.

JUNE 23, 1904. BALDWIN BURNER. FUEL—OIL.

Time of run	3 hrs., 35 min.
Feed water	14,755 lbs.
Weight of oil	1,434 "
Temperature of feed water	73° F.
" of oil	152° F.
Pressure of steam	125 lbs.
" " " (burner)	60 "
" " oil "	Head.
Calorimeter temperature	214° F.
" pressure	2¾" water.
Lbs. of water evaporated per lb. of oil	10.3 lbs.
Factor of evaporation	1.192.
Equivalent evaporation (from and at 212° F.)	12.27 lbs.

TABLE OF SUMMARIES.

Name of Burner.	Steam Gauge Pressure.	Quality of Steam.	Temperature of Feed Water.	Lbs. of Oil per Hour.	Lbs. of Water per Hour.	Lbs. of Dry Steam Evaporated per Lb. of Oil.	Equivalent Evaporation from and at 212° F.	Date of Trial (1904).
National oil burner.	85	96.1	60° F.	160.2	2133	12.75	15.24	April 16
Sheedy Garrick.	100	95.7	66	333.8	3742	10.75	12.84	May 19
"	100	95.7	66	311	3460	10.75	12.84	" 19
"	96	95.7	68	312	2965	9.095	10.84	" 27
"	100	95.7	68	389	3872	9.095	10.84	" 27
"	110	96	73	351	3280	8.99	10.55	June 1
"	108	95.5	73	364.6	3333	8.99	10.55	" 13
"	108	95.5	73	332	2600	7.48	8.905	" 21
"	100	95.4	73	360	3032	7.48	8.905	" 21
Baldwin Locomotive.	125	95.3	73	400	4120	9.82	11.7	" 23

Name of Burner.	Oil Burnt per Hour per Horizontal Square Foot of Fire-box (Pounds).	Oil per Hour per Square Foot of Heating Surface (Pounds).	Boiler Horse Power.	Percentage of Molasses to Oil.	Lbs. of Molasses per Hour.	Lbs. of Dry Steam per Lb. of Molasses.	Equivalent Evaporation From and at 212° F. per Lb. of Molasses.	Date of Trial (1904).
National oil burner.	6.56	1.25	70.9					April 16
Sheedy Garrick.	13.50	2.513	124.0					May 19
"	12.58	2.420	114.6	19.3	61.2	1.505	1.795	" 19
"	12.60	2.430	98.5					" 27
"	15.75	3.035	128.0	27.4	106.5	1.35	1.61	" 27
"	14.21	2.732	107.0					June 1
"	14.75	2.840	109.3	22.9	81.0	1.263	1.50	" 13
"	13.42	2.590	85.7					" 21
"	14.56	2.800	99.3	47.5	171.0	1.17	1.39	" 21
Baldwin Locomotive.	16.20	3.120	136.0					" 23

Six bricks were removed from the front of the fire-box leaving an air space of 210 square inches underneath the burner. It was

found to be impossible to deflect the burner downward to such an extent that the flame would strike the floor before reaching the bridge wall, owing to the upward direction given to the steam by the sloping plate at the mouth of the burner; for this reason but few of the fire bricks were thoroughly heated, so that perfect combustion could not be secured. The Baldwin burner is only adapted for use below the mud ring.

Before the start of the test the fire-box was thoroughly cleaned out but the tubes were not touched. From this point to the tenth

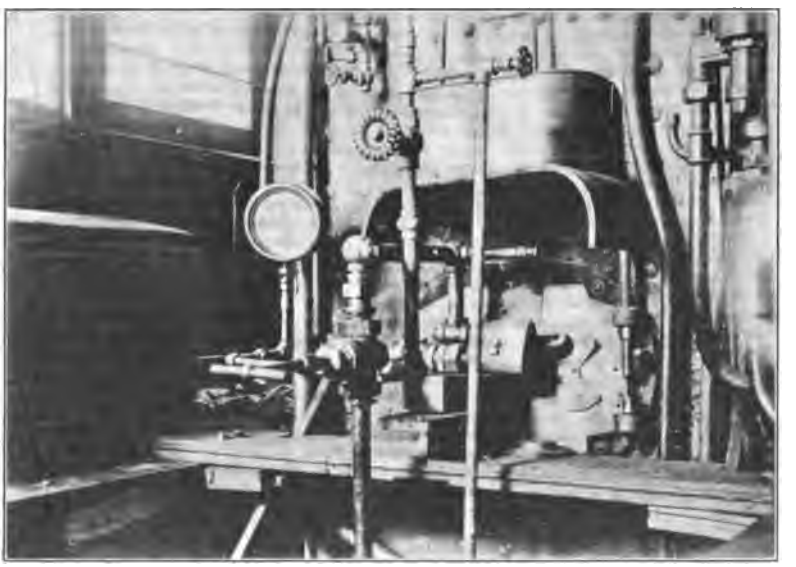


FIG. 12.

test the fire-box was not again cleaned. The character and amount of soot accumulated was carefully noted after each test and also the effect of such accumulation on the evaporation of water.

The soot observed after the oil test was a deposit of fine black carbon, but after the molasses test this was found to contain an appreciable amount of a whitish ash. A preheating of about 130° F. rendered the molasses sufficiently fluid to obviate clogging in the burner, and also facilitated the atomization.

From the foregoing test and other available data on the subject, we conclude that molasses may yield an evaporation of 2 lbs. of water per pound of molasses under proper conditions. Throughout the test the oil in the molasses run was assumed to have

the same efficiency as in the preceding oil test, whereas in fact it would be lower owing to the accumulation of soot.

At present the method used for disposing of the molasses is to sprinkle it on the bagasse after it leaves the last mill on its way to the furnace, in the proportion of 50 lbs. to the ton of cane ground, or in the ratio of one part of molasses to five of bagasse. It is doubtful if it would pay to spray the molasses on to the burning bagasse since the steam used for atomizing would represent a large portion of the steam generated by the molasses, an item which does not occur in the present method of sprinkling on the bagasse; however, in factories using the diffusion method of extracting the sugar, which embraces beet sugar houses, where there is no bagasse this method of disposing of the molasses (*i. e.*, spraying on to a coal fire or burning with oil) could be used, if the price obtainable for molasses did not surpass its value as a fuel.

Molasses has been burned as a fuel in Hawaii, Java, Cuba, and Egypt. The more sugar extracted from the molasses the less its usefulness excepting for fuel, for the manufacture of alcohol and for feeding of cattle.

(*a*) To the Standard Oil Company acknowledgement is due for their courtesy in supplying all the oil for these tests, as well as for the loan of the Sheedy Garrick Burner used in tests 2 to 8, inclusive.

(*b*) Acknowledgments are also due to the Baldwin Locomotive Works of Philadelphia; The National Oil Burner and Equipment Company of St. Louis; The Tate Jones and Company of Pittsburgh, and The International Gas and Fuel Company of Chicago for their assistance in supplying burner and apparatus necessary to this investigation.

(*c*) Data for this thesis has been drawn from "The Report of the Hohenstein Boiler and Liquid Fuel Boards, 1902"; W. H. Booth on "Liquid Fuel and its Combustion"; *The Journal of the Hawaiian Sugar Planter's Association:* and *The Louisiana Planter.*

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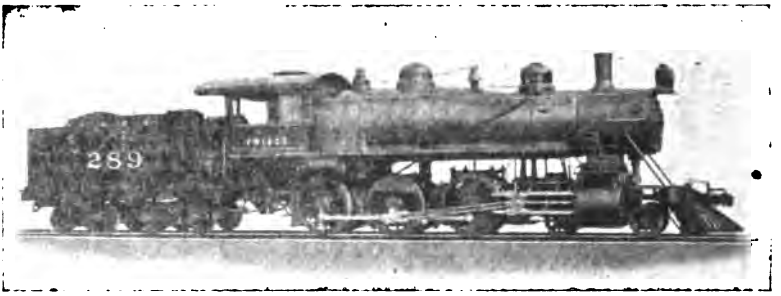

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VOL. XXVI. JULY, 1905. No. 4.

OUTLINE OF WORK OF THE TOPOGRAPHIC BRANCH OF THE UNITED STATES GEOLOGICAL SURVEY

WITH DETAILS OF SECONDARY (PLANE TABLE) TRIANGULATION.

BY JOSEPH A. CLOSE, C.E.

The United States Geological Survey, in the Department of the Interior, was created by Act of Congress approved March 3, 1879 (ref. 1).

At present it is organized in five great branches: (1) administrative, (2) geologic, (3) topographic, (4) hydrographic, (5) publication.

The topographic branch, as its name indicates, is engaged in making a surface map of the country.

The uses of such topographic maps are many. For the purposes of the national government and the state they are invaluable, as they furnish data from which may be determined the value of projects for highway improvements, for railways, for city water supply and sewerage, and for the subdivision into counties, townships, etc. They serve the military departments of the Government, National and State, in locating encampment grounds, in planning practice or actual operations in the field, and, during war, in indicating the precise situations of ravines, ditches, buildings, etc. The Post-Office Department utilizes them in considering all problems connected with the changing of mail routes, star routes, and especially in connection with contracts and assignments of rural

free-delivery routes. As the outlines of wooded areas are to be indicated on these maps, national and state foresters will find them invaluable as a base for classifying the wood-lands and recording the nature and quantity of the various trees and the relation of the wooded areas to highways of transportation, as railways, streams, etc. These maps are, of course, essential to detailed geological studies and to investigations concerning mineral resources, water power, and land reclamation.

The states of Massachusetts, New Jersey, Rhode Island and Connecticut have been finished in coöperation with those states, and at present coöperative topographic work is progressing in New York, Pennsylvania, Ohio, West Virginia, Maryland, Maine, Kentucky, Alabama, Louisiana, Michigan and California.

The general plan adopted for mapping the United States consists in dividing the country into quadrilateral areas (called "quadrangles" or "sheets") bounded by parallels and meridians of latitude and longitude.

Three regular scales and a series of special scales have been adopted. For reconnaissance maps in the rougher portions of the Far West and Alaska the scale of 1 : 250,000, or nearly 4 miles to the inch, is standard. For the general map of the United States the scale of 1 : 125,000, or nearly 2 miles to the inch, is standard. In the more densely populated districts — the Atlantic coast, parts of the central region, and portions of the Pacific coast — the scale of 1 : 62,500, or about 1 mile to the inch, is standard. Special larger scales, from 2,000 feet to the inch up to 100 feet to the inch, are used for detailed surveys of important mining regions, for planning and construction of irrigation projects, etc.

These maps are printed on sheets approximately 13 by 17 inches. The area represented on the 1-mile scale is 15 minutes of latitude and 15 minutes of longitude, or, on the average, about 225 square miles; on the 2-mile scale, 30 minutes of latitude and 30 minutes of longitude, or about 1,000 square miles; and on the reconnaissance or 4-mile scale, 1 degree of latitude and 1 degree of longitude, or approximately 4,000 square miles. An atlas sheet is known by the name of the most important town, city, or natura feature within the quadrangle represented.

The field work is ordinarily done in six different stages: (1) primary triangulation, (2) secondary (plane table) triangulation, (3) primary levels, (4) secondary (flying) levels, (5) road traverse, and (6) sketching.

Primary Triangulation.

Most of the primary triangulation of the geological survey is based upon the triangulation of the United States Coast and Geodetic Survey. In the Appalachian Region this network is expanded from the United States Coast and Geodetic Survey base lines used in determining the "Eastern Oblique Arc of the United States" (ref. 2), namely: the Epping base (5½ miles) near Cherryfield, Maine, the Massachusetts base (10¾ miles) near Providence, Rhode Island, the Fire Island base (8¾ miles) on Fire Island, N. Y., the Kent Island base (5½ miles), Maryland, the Atlanta base (5¾ miles), Georgia, and the Dauphin Island base (6½ miles), Alabama. These lines were measured from 1834 to 1872 with either the Hassler or Bache-Wurdemann base bars (refs. 3 and 4).

In this region the geological survey has measured one base line with a 300-foot steel tape near Hillside, Westmoreland County, Pa., as a check on distances developed from the coast survey line, Maryland Heights — Sugar Loaf. This triangulation has now been connected with the systems along the Mississippi and around the Great Lakes, which are based upon lines ran with more improved base bars. Bases are now generally measured with either the iced bar, designed by Prof. R. S. Woodward, or by steel tapes (ref. 6).

In advancing the triangulation, points are selected (refs. 1, 5 and 6) from 5 to 25 miles apart, generally on the highest points, so that at least two may be plotted on each sheet, although not necessarily within the boundaries of the sheets themselves. These are marked with an iron post, a copper plug set in solid rock, or a bronze tablet, countersunk and cemented in either solid rock or in the center of the top of a stone post, at least 48 by 8 by 8 inches, set flush with the surface of the ground. One or more reference marks such as crosses or holes cut in rocks are usually located from 20 to 200 feet from the station.

Most of the signals are quadripods made of sawed timber and centered over the station. If a tree is near the highest point it is often used for a signal and the station mark set near it. Sometimes the tree itself is taken as the station mark. This necessitates the calculation (ref. 7) of reduction to center, but saves the cost of erecting a quadripod, which will last but a few years. A tree is a much better signal at a long distance or on a hazy day.

The point is located by reading the angles formed by it and two

or more known points by the use of a theodolite having a circle of 8 inches in diameter, graduated to 10 minutes, and reading by 2 micrometer microscopes to 2 seconds. The resulting triangle or triangles are solved and the latitude and longitude ascertained to .01 of a second, and also the distance between the points. Prominent points, such as a church spire, a standpipe, or a lone tree, are sometimes located by angles read on them from other stations

"Owen," Otsego County, N. Y.

Quadripod of sawed timber, centered over station, as used by the primary triangulation men. The two targets on center pole are covered with white cotton cloth.

Top of station mark just showing above ground.

without occupying the points themselves. Astronomical observations are taken at some of the stations as checks.

The primary men also locate a true north and south or meridian line in every county seat to be used by the county and local surveyors in determining the declination of their compasses at any time. These lines are usually marked by tablets set in stone posts similar to those used on primary triangulation stations and placed from 300 to 500 feet apart.

Plane Table Triangulation.

The second stage of the work is known as the secondary or plane table triangulation or control. This sometimes follows the primary work directly, but more often is two or three years after.

On receiving his orders, which simply tell him to report at a certain place where he will find his instruments and to do one or more sheets which will be named, the plane tableman will get every map possible of the locality in which he is to work that will be of use to him as a guide map. County clerks and postmasters can usually give some information in that line. In some places fairly good county atlases are obtainable and drainage maps of coal, oil, or water supply companies are often available. Even in the poorest countries the post-office map is of some use and at times the only one to be had. From these maps a guide map is made, unless one can be obtained which will answer the purpose, showing, if possible, the drainage system, highways, railroads, and towns. On it is drawn temporarily the five minute projection lines.

From this map will be chosen the place which will be used as headquarters for the sheet. This will generally be the largest town or city near the center of the sheet connected by railroad and telegraph. The larger the place, the better, as a rule, will be the hotels and liveries. Supplies may also be more readily and cheaply purchased.

On arriving at the headquarters the hotel and livery will be looked after and, if satisfactory, the instruments will be unpacked. These will consist of a plane table board, 24 by 31 inches, a Johnson tripod, a long telescopic alidade, a compass, a plotting scale, a metallic tape and a pair of field glasses. These will also be a leather and possibly a waterproof case for the board and a wooden case containing the blank plane table sheets. The following outfit will also be needed and if not furnished will be purchased: a large umbrella with an iron pointed staff and connections, an ax, a hatchet, and a double-edged saw such as is used for pruning fruit trees. The last three will be protected by leather cases. A pair of tree climbers and a pulley with about 200 feet of rope for hauling flags to tops of trees will be needed. A large leather gunners' haversack is useful to carry part of the outfit when on foot. A small bag is needed to hold nails when in tree tops and also a canteen and haversack, as lunches are usually eaten in the

field. A screw driver and monkey wrench will be found handy in case of breakdowns on the road. Besides this permanent outfit there will be bought from time to time, as needed, signal cloth, nails, wire, and cord. Shot bags are very convenient for holding nails and can usually be obtained where the nails are bought.

The plane tableman will have one regular assistant and at times may require the services of a guide and axmen who will be hired when needed. The regular, or station assistant, as he is called, may be assigned for the work from a list of applicants in Washington, but is usually hired by the plane tableman. His qualifications depend somewhat on the nature of the country to be worked. Should it be sparsely inhabited and heavily timbered so that the number of control points will be small, he will be needed more as a teamster and axman, the observer taking his own notes on stations. In more thickly settled and highly cultivated country, where 50 to 100 shots may be taken from a station, he must be able to record quickly and accurately the descriptions of points as dictated. In any case, he must have the strength and nerve to climb the highest trees either to place flags or to clear a line of sight even in a high wind. He is usually hired when the work is started so that his knowledge of the country may be of service while he is learning his other duties. If satisfactory, he is then kept for the full season, as his knowledge of the work will outweigh other considerations.

Before starting in the field work the instrument will be looked over and if any damage has been done in transportation that cannot be repaired on the spot a duplicate part will be telegraphed for. The plane table sheet will next be examined. This will be a piece of heavily mounted and thoroughly seasoned paper cut 24 by 31 inches to fit the plane table board. On it will be plotted the 5 minute projection lines to the scale of 1 : 45,000, if a 15 minute sheet, or the 10 minute lines to the scale of 1 : 90,000 if a 30 minute sheet. This will leave a good margin outside of the boundaries of the work. If the primary work has already been done, the primaries that can be plotted on the paper, whether within or without the boundaries of the sheet, will be put on with reference to the projection lines. There must be at least two intervisable points. A description of the points similar to that given below will be furnished and the points checked by the latitude, longitude, and distance between them.

"Writer," Orange County, N. Y.

On a brushy ridge in Mount Hope Township, three miles southwest of Otisville station, on Erie railroad, on land owned by Mr. Writer, proprietor of the Writer House, Otisville. Tenant lives 400 yards east of station. The ridge is cleared on eastern side, giving a good view in all directions.

Station mark: A copper bolt one inch in diameter stamped "U.S.G.S.," set in solid rock.

Reference marks: Inch hole drilled one inch in ledge; azimuth, 148°; distance, 29.90 feet. Inch hole drilled one inch deep in ledge; azimuth, 16°; distance, 30.31 feet. Inch hole drilled one inch deep in ledge, south end; azimuth, 230°; distance, 44.80 feet.

[Latitude 41° 26′ 27.34″ Longitude 74° 34′ 28.46″]

To Station.	Azimuth.			Back Azimuth.			Log. Distance.
	°	′	″	°	′	″	Meters.
High Point	28	45	25.1	208	41	57.3	4.1818277
Roads	158	28	59.5	338	27	00.6	4.0548316
Wolf	177	14	34.5	357	14	10.5	4.2408390
Vernon	211	49	25.0	31	51	46.7	3.9735791
Houston	253	18	36.1	73	27	08.3	4.2725795
Eve	319	07	01.4	139	13	21.5	4.3105577

The plotting will probably be found to be correct as the points have been checked before being sent into the field. In case they have not been plotted they will be as soon as the descriptions are received and if, after plotting by latitude and longitude, the distance between points does not check, it is reported immediately.

The positions of the primaries will now be plotted on the guide map with reference to the temporary projection lines.

The first field work will be to flag the primaries. If, as usual, there are more than two that are intervisable, the one from which the most primaries may be seen and giving the best angles between them will be left till last. On arriving at the first station to be flagged, the signal, if the usual quadripod, may be found to have been blown down and may have disappeared entirely. In that case it will be rebuilt as solidly as possible and anchored down either with rocks or logs. The flagging material will be put on in such a manner as to make the signal as conspicuous as possible. It will be of the strongest unbleached white cotton and turkey red cloth cut in two yard strips and placed as may be seen in the accompanying illustrations. On quadripod signals the cloth on

the base is of the most value, especially at long distances, as it is always spread out so as to reflect the sun when the flags on the pole might be hanging loose due to lack of wind. The turkey red is placed at the top of the pole for two reasons: (1) On a hazy day it can be seen better than the white, and (2) it forms a sharp line on which to read verticle angles instead of reading them on the ground. In order that the flag may be of use in the latter

"Tassel," Oneida County, N. Y.

Quadripod reflagged and ready for secondary triangulation work. Plane table and umbrella in position.

Top of flag above ground 28 feet. Station mark and four granite witness marks of New York State Survey showing above ground.

case the elevation of the top of the flag above the ground is always measured and recorded. Red is used rather than black since it is fully as dark and can, moreover, be seen against a green background.

Should the signal be a lone tree on the highest knob in the vicinity no marking other than placing a strip of white around the trunk is necessary. Should, however, it be on a low hill so that

looking down on it, it would have a green background, or should there be surrounding trees, it will be flagged, for it is poor economy to only half mark points. In tree flagging the assistant will climb the tree with the rope and saw. When at the top he will lower one end of the rope and begin clearing what branches will be in his way when handling the flag. In the meantime the plane tableman will get the tallest pole that is light enough to be handled,

"Arnett," Doddridge County, W. Va.

Quadripod with tall flag to be seen above surrounding peach orchard and cornfield. Top of flag above ground 45 feet.

probably from 25 to 40 feet long, and nail on the cloth. If the butt is too thick it will be flattened and a 60 penny nail driven partially through it. The pole will then be measured and its length recorded. The pulley, hatchet, and nails will now be hauled up by the assistant. The pulley is firmly fastened as high as possible, the rope run through it and both ends let down. One end will now be fastened to the butt of the pole and a section of rope laid

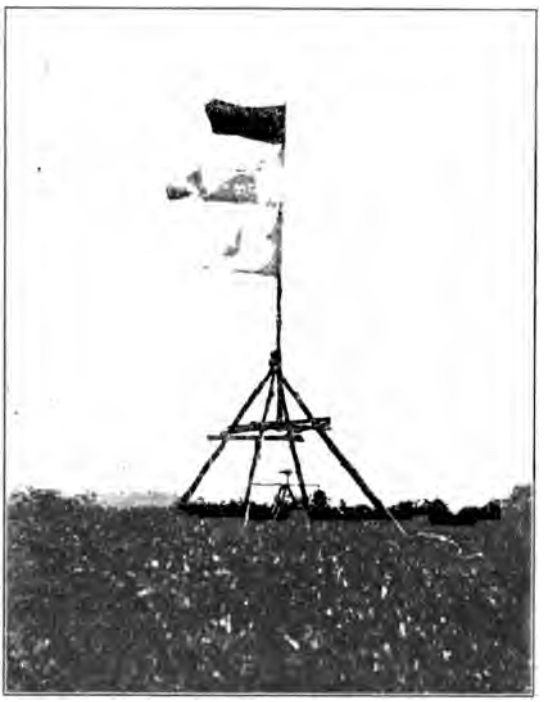
along the lower two thirds of the stick and fastened by a piece of rope having a length of 3 or 4 feet. The pole is now straightened up against the tree trunk and hauled up slowly, top first. The plane tableman will do most of the pulling and must be able to hold or fasten the rope should it become necessary to stop to untangle the flags. When the rope tied around the upper part of the pole comes to the pulley, it is undone and fastened loosely

"McCarty," Herkimer County, N. Y.

Low quadripod, partially of sawed timber as erected by plane tablemen. Four legs of quadripods were driven one to two feet in the ground and three-foot braces driven in and nailed at right angles to their bases.

around both tree and pole at the highest part of the tree. Now comes the hardest part, for by this time, part of the flag is above the tree, so that the wind may cause considerable pressure on it. If the wind is blowing hard another rope will be tied loosely around the tree and pole a little above the butt. The pole will then be slowly, foot by foot, hauled as high as desired, raising the

lower rope when necessary, and the butt nail driven. The pole will then be made vertical and *securely* fastened with nails, and, if necessary, rope, or better, wire, so that it cannot be blown from the tree. Any branches, whether on the flag tree or surrounding trees, which will interfere with the flag being seen will be cut. Before the rope is dropped it is used to measure the distance from the butt of the flag pole to the ground.



"Writer," Orange County, N. Y.

Quadripod of rough timber erected by plane tablemen on solid rock. Anchored by heavy rocks on cleats nailed to base.

Base covered with white cotton cloth after picture was taken.

Top of flag above ground 20 feet.

While the assistant is finishing the flag the triangulator will spread out his guide map on the ground or some flat surface and orient it with his compass, allowing for the declination. He may now get a good idea of the country he has to work and possibly, by the aid of his field glasses, pick out some of the other triangulation points. At any rate he can decide on points where he will

later put up flags. A short description will be made of them and their approximate location fixed on the guide map. If the position of the primary, which has been plotted with reference to the temporary projection lines, is not where it should be on the guide map, it is changed. This is done on each primary and then the projection lines drawn permanently with reference to the primary locations.

On going to the last given point, which has been previously

"Cherry Hill Flag," Minisink Township, Orange County, N. Y.

Tree marked by flag and cloth on trunk. Is situated on low hill with other trees near by.

Top of flag above ground 27 feet.

selected, the instrument will be taken along for the best checks of the plotting on the sheet. The table is set up as near the station mark as convenient and leveled by use of the striding level from the alidade. If it is at all windy a weight will be suspended from the head of the tripod to steady the plane table and prevent accidents.

If the sun is bright the umbrella is set up to protect the eyes and paper. After the alidade and paper have been cleaned from sand, grit, or insects, the adjustments for collimation and parallax will be looked to. Then the thick edge of the alidade is placed over the center of the needle pricks representing the occupied station and the most distant primary, and the table turned until the cross hairs intersect the signal. This is called *orientation.* The table will now be clamped firmly and the alidade placed over the other plotted points. If the signals come in exactly on the cross hairs, as they should, the plotting of the occupied point is correct, as is probably the others.

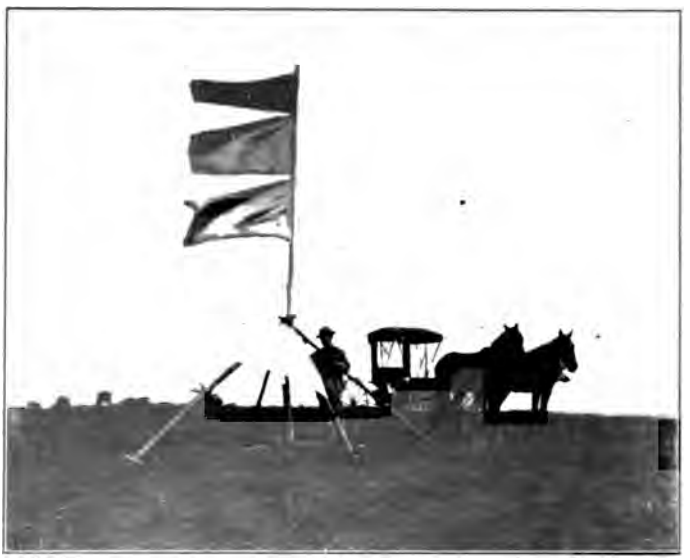
The true magnetic declination can now be obtained by the compass and shown on the sheet by placing one edge of the south end of the compass box over one of the intersections of the projection lines, and, when the compass reads north, drawing a line along the box.

If the triangulation is to be started from this station nothing more need now be done with the instrument until the flagging is finished. If, however, it is desirable to start the work from some other primary it is a good plan to draw short lines at each end of the alidade when it is sighted at the other points and is over the points representing them on the sheet. The reason for this is that since this point has been selected as the best located to check the points, the orientation is probably the best obtainable and the table may be brought in this same orientation much more surely by using these lines at the furthest possible distance apart rather than the plotted points themselves, which are at much less distance.

By this time a good idea of the country has probably been obtained and some plan of work formed. In a sparsely settled and heavily timbered country fortunately few control points, not more than three or four to the 5 minute block, are needed. Under such conditions there will probably be almost nothing that can be used as a triangulation point, so that flags are erected. A number of the highest points will have been noted and their positions approximately determined on the guide map while flagging the primaries. For this kind of work it may be found more convenient to go in the saddle and so save considerable walking.

If any cleared or partially cleared knobs have been seen, they will be visited and if it is possible to make a location there from the primaries or by the use of other flags to be put up later, it will be marked. If the hill is cleared, a quadripod flag may be erected.

This is done by first driving a large stick solidly into the ground and nailing the flag pole to it. Four braces, sharpened at their butts are driven into the ground and their tops nailed to the pole and together and either tied with cord or wired. Short braces are driven solidly into the ground at right angles to and at the foot of the main braces and spiked. The tops of the main braces are sawed off so as not to interfere with the flag. In case the point is a high one so that there will be considerable pressure on the quadripod, the main braces may be stiffened with horizontal braces



"West Edmeston Flag," Otsego County, N. Y.

Quadripod flag, showing driven post, main and foot braces, and cloth on base.

connecting them. While cloth is then placed around the frame and securely fastened. In case it is impossible to drive the braces into the ground the signal must be weighted down with either rocks or heavy logs. Its height will be measured and its position located on the guide map.

If the map does not show enough to make a location from itself, it is oriented by use of the compass and the point located by rough resections from those points that are in sight. A record will be made, before leaving the hill, giving the height of the flag and the names of all flags or marked points to be seen from it. Next the

timbered points which have been noted, will be gone to. The observer will first find out, from a tree top if necessary, if the hill is the highest in the immediate vicinity, and if so, whether the point can be located, if flagged. If possible, the flag tree will be selected so that, if required, a station can be made at this point. Unless it will require too much heavy cutting, it is better to have the station on the ground and therefore a tree near the highest point of the knob is selected if the flag can be set high enough to be seen over the rest of the trees. If the knob is heavily timbered and one of the tallest trees is a large one, so that a platform can be built in the top solid enough to hold the instrument and observer without swaying, it may be selected.

Flagging under such conditions is hard and slow work, oftentimes not more than two or three signals being put up in a day. This is due to the fact that traveling is difficult and that often, before a suitable hill is found, two or three others may have been climbed only to find higher ones near by shutting off the view.

While these flags are put up primarily so that they may be easily located and so as to give the required number of points evenly distributed over its sheet, it will be born in mind that one of their principal uses is to control the traverse and that when possible they are located so that they may be seen and intersected by the traversemen from the roads.

Should the sheet be so heavily timbered as to require the kind of flagging over its total area as has just been described, the chances are that there may be considerable timber on the primary hills themselves. Fortunately in such a country, timber will be cheap and when on the highest points, so inaccessible, as to be almost valueless. Probably a good deal has been cleared by the primary men but seldom all that is necessary. In this case the owner will be seen and if possible, hired to do the required cutting. They are usually glad to be paid to clear their own land. It will be found much cheaper to hire axmen than to use the time of the plane tableman and his assistant. The clearing will be done immediately in order that the signals may be easily seen when the rest of the work is being flagged.

The above applies to sharp knobs that can be cleared in a reasonable length of time. Should, however, the knob be flat, or there be much objection to clearing it, it is cheaper and easier to build a tower of rough timber high enough to see over the obstructions, if it is necessary that the point be occupied.

It may be, however, that the country to be mapped is thickly settled and highly cultivated, with little or no timber. In this case the work is of an entirely different character. Instead of 30 to 40 points controlling the sheet, 150 to 200 may be located, the majority of them being buildings and lone trees, flags being put up to mark the positions of subsiderary stations or upon prominent timbered hills, if any, not only to locate them, but to enable the triangulator to work around them, as they may cut off the view of some of the work from the rest.

At first, as in the former case, substantial signals will be erected, the more conspicuous the better, on the primary triangulation points and on other prominent hill tops. In doing this work as many different roads as possible will be driven over in order to familiarize oneself with the topography of the country; to pick out the best secondary stations, flag them when not marked by trees or other objects easily seen and identified, and locate them on the guide map, and to fix in one's mind peculiarities and location of objects most likely to be seen from the stations thereafter occupied.

After the sheet is well signaled a list of all the flags to be seen from each of the primaries will be made out, also their approximate location lightly marked on the plane table sheet.

The first station will now be made and one of the most prominent triangulation points, located preferably in the southern part of the sheet is chosen, so that when the majority of the sights are taken, the observer will be looking away from the sun. In this way objects are more clearly seen and peculiarities noted. Clear atmosphere is *essential* when the first stations on the sheet are made. In fact, if when the work is being done, most of the days are smoky, hazy, or rainy, the first clear day after the primaries have been flagged will be used, even if the sheet is not completely flagged, provided, of course, that there are enough other points to be seen besides the flags. Then, when the flagging is finished, the station will be reoccupied and the flags cut in.

The instrument will be set up and oriented as when the plotting was checked. First, foresights are taken to signals and then, starting so that the sun may be shining on the side of the objects nearest the station while being sighted, a circuit of the horizon made, taking foresights to all prominent objects, such as cupalos, towers, chimneys, flag poles, monuments, church steeples, school

houses, houses, barns, wind-mills, trees, hill tops, spurs, etc. These points are found best and their characteristics noted by using the field glasses. In sighting at buildings it is best to take a chimney, cupalo, or peak of roof at, say, the north or east end on every occasion, as it may happen that a shot may be taken at the same object from a different station without recognizing the point and a third shot will be found to go through the intersection of two others, and, on looking up the descriptions, they will be found to be the same object.

The lines of sight will be drawn with a 9 H pencil, sharpened to a chiseled edge, at considerable length along the thick, fiducial edge of the alidade, care being taken to always hold the pencil at the same angle and see that the contact of the rule and the paper is perfect. On all foresights to points which may afterwards be used as stations, in addition to the regular line, short lines are drawn at each end of the alidade in order to get the best possible orientation when sighting back towards the first stations.

From time to time while making observations and upon completion of the work of each station, the original orientation will be checked to see if any movement of the table has occurred. This is always done in case the table is jarred while moving about.

The stations are designated by Roman numbers I., II., III., etc. Each sight has a number beginning at 1 on each station. All the sights to the same object from other stations will retain this number and the object will be known by it during the progress of the work. Therefore a note taken at station X., reading "Flag 3–27," means that a flag whose description will be found in the notes taken on station III., and which was the 27th shot from that station, was also seen from station X.

The number of the sight and a partial description is written on the main line and the number written on the short orientation lines and connected by an arrow so that there may be no confusion when lines come close together. The numbers and descriptions are written with a sharp pointed 9 H pencil. Small sand-paper pads are always carried and used frequently to keep the pencils in good condition.

Full descriptions are made of all objects sighted and recorded in the note book. Time and space are saved by using abbrevitions such as N. S. E. and W. for the points of the compass; T. K. (top knot) for cupalo or ventilator; and Ho. for house. They are

understood by both observer and recorder so another person can take up the work of either. Exact grammatical English is not always used, for an object noted as "T. K. Bug Ho." is as fully described and probably will be better remembered than if it were written, "Cupalo of New York State Hospital and Insane Asylum." Care is taken to get all the churches and school houses possible, for, not only are they easy to identify by both plane tableman and traverseman, but because as a rule they are situated at street or road crossings or intersections and so give best control for the traverse work. Azimuths of long, straight stretches of roads, railways and shots at road intersections are taken and their approximate location marked whenever possible even when they cannot be located. The observer will practise estimating distance and as soon as locations are made is able to verify and better his approximations.

After all the sights have apparently been made, the striding level is adjusted and the ground gone over again to fix the relative positions and characteristics of the points indelibly in the mind and to take vertical angles to the points whose elevations are required. The value of having the red cloth on flags can now easily be seen for it forms a definite line at which observations are taken, as it is exceedingly difficult to tell within three or four feet where the surface of the ground is at a distance of five or six miles. If sighting at a hill higher or lower than the occupied point, the surface appears highest either toward or beyond the summit, as the case may be; grass, brush, and trees also interfere and sometimes make its determination impossible. Good elevations may be obtained up to five miles but beyond that they are of little value and are only used as rough checks.

The next primary is now visited. Shots are taken at all flags or marked points which may be used as stations and the orientation lines drawn. Should any of these be points at which shots were taken from the last station, a light circle is drawn around the intersection of the lines which marks the location of the point. The field glasses will then be used to try and identify any points that may be in sight which were sighted at the other station. The descriptions are read to aid the memory. After that, new shots are taken, and the angles read.

Four "magnetics," one to each quarter, are an taken on each sheet and should this and the other primaries be situated to fill this requirement, they are taken from these points.

If there are any more primary points they will now be occupied, and, after the work on them is finished, the first subsiderary station will be gone to. It will be a point, if possible, visible from at least two primaries from which shots have been taken to it. The alidade will be placed on the orientation lines, coming from the most distant station, in the reverse position to that it held when the lines were drawn, and the table oriented on the signal and clamped. The alidade will now be placed on the other orientation lines drawn to the occupied point and if the signals show on the cross hairs of the telescope, the point is not only accurately located at the intersection of the lines but the orientation of the table when the sights were taken on the primaries is proved to be correct. All other located points in view are sighted not only to prove the station but the location of the points themselves. The point is marked by a small hole made by a number ten needle. A small triangle is drawn around it and the number of the station marked along side of it.

A number of needles, as many are lost or broken, are made by forcing all but about one fourth of an inch from the point of the needle proper into a piece of sealing wax about three sixteenths of an inch in diameter and one inch long. A few of these may be carried by being stuck through the hat band, and extra ones in a small box.

The work now proceeds as from the former stations. Points are considered as located and are marked by a needle point when three or more shots at good intersection angles have been passed through them. A point is really located by two shots, but its location is rarely accepted until a third check shot has been obtained unless there are other control points near and there has been absolute certainty as to the identification and the correctness of both of the shots.

In many cases the primaries are located at the highest point of a long ridge or on the highest of a number of hills. In such cases it often happens that a point from 1½ to 2 miles distant may be found, which although not as good as the primary itself, still gives an excellent view of practically the same objects and from nearly the same view point. When the primary is flagged if it is found that many long shots, *i. e.*, from 10 to 18 miles, will be taken to objects such as houses or barns whose position it is desirable to determine by prosection, but there is doubt of their being recog-

nized from other stations, since they cannot be easily seen or remembered due to the distance, the nearby point will also be marked. If possible this station will also be occupied on the same day as the primary and so intersections may be obtained for nearly all the long shots. These intersections will necessarily be acute, but they will materially aid in the identification of the point from other stations. The point, however, will not be occupied until an

"Small Knob Flag," Orange County, N. Y.

"Baby" tripod flag used to mark highest point of a high, perfectly cleared knob of Shawangunk Mountains near Port Jervis, N. Y.

Top of flag above ground five feet.

orientation line from some distant primary, in addition to one from the nearby one, has been obtained.

In driving to and from stations the observer is always on the lookout trying to recognize his points and pick out new ones. The ability to instantly recognize and locate points, although they may not have been seen for some time, requires constant practice and considerable skill and is of immense value in order that quick work may be done.

If possible, the work is so arranged that in the morning stations are occupied having most of the work to the west and in the afternoon, those looking to the east.

Exceptionally clear days are spent on stations from which long sight work may be done.

The location of stations is not restricted to places which have been previously flagged. Foresights may be taken to trees, bushes, fence corners, barways, stumps, rocks, chimneys of buildings, etc., on tops or sides of hills and the points gone to. The

"Sanger Flag," Waterville, Oneida County, N. Y.

Plane table outfit in action beside of a quadripod flag in an oat field. Timber showing to rear cuts off the view in that direction.

advisability of flagging most of the stations before beginning the triangulation is now easily seen. It requires considerable practice to go to a point which may only have been noticed at a distance of ten miles, and, even when the point is reached, to recognize it. What was thought to have been a bush on the summit of a hill may have been a tree top showing over it. Animals, lying down, often at long distances resemble stumps or rocks. The time lost on exceptionally clear days in hunting for points, which, had they been flagged, could have easily been gone to, is almost invaluable.

Beside this the correct orientation depends wholly on one shot, although it is checked by resections. On arriving at the point, it is often found that it is not easily accessible or favorably located for a good station, but that a good one may be made in line with it and the station from which the shot was taken. If such a point is obtained, that is, a point in line and also visible from at least two other located points, the table is set up and oriented on the former station and clamped. The alidade will now be pointed at some other located point, and when it is over the point on the board representing it, a line is drawn intersecting the line drawn at the other station to the point now occupied or in line. This is called *resection.* The intersection of the lines is the point occupied. This is always checked by resection from another point if possible. As has been noted, two points, if correct, make a location, but triangulation of this kind is not guess work and all points should be known to be correct beyond doubt. Even the point so obtained may not be on the top of the hill and although some work may be done, it is often desirable to get higher up to get other shots. This may be done by sighting at some definite point, whether located or not, the further off the better, situated in line with the occupied point and the point at which it is desirable to make a new station, and drawing sight lines at each end of the alidade and back from the occupied point (since the object sighted must be in the opposite direction from the summit of the hill which cannot be seen over). The new point is marked and the distance to it measured and plotted on the line but *only* as a check. The exact location is determined by setting up over the new point, orienting on the object taken and resecting from the station and two located points used in locating the point on the side hill. The side hill point having been marked, the lining in is checked by depressing the telescope after sighting at the orientation point. Accurate locations may be made in this manner and new shots taken from such a station, provided great care is taken in its location. If shots are taken to new stations from such a point its exact location is marked by a flag in order to sight back to it. If, however, it has only been used to locate points from old shots or to take shots at buildings, etc., which will not be used as stations, a nearby tree may be located by sighting to it and measuring the distance so that it may be used as a simple control point, without spending the time in erecting a signal.

The time and labor used in clearing obstructions to get sights at ordinary control points is often saved by moving about a station in this manner, but shots to points to be used as stations are always taken from the signaled point.

Shots to new stations should never be taken to points at a distance greater than that of the point upon which the orientation of the occupied station depends. If this rule is disregarded, there is always a chance that the sheet may be "swung," and so cause the worst error a plane tableman can make.

It is often possible to make locations at points to which foresights have not been taken, but points so obtained should only be used for the locations themselves, except possibly to verify other points. New stations should never be made from them, for although a perfect location can be made, it is not certain that the orientation is absolutely correct.

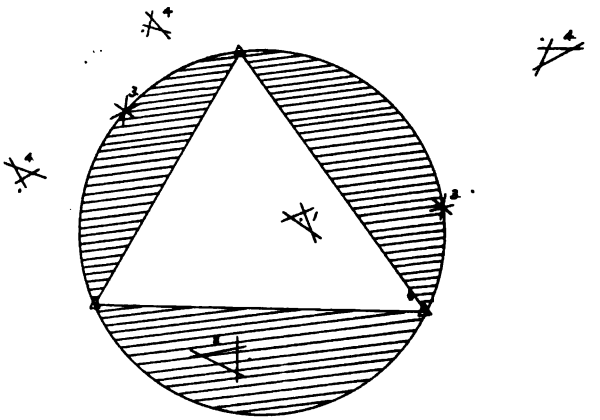
When it is possible to get in line with two located points, we may orient by sighting on them and locate by resection from a third point.

It is also possible to make a location, or rather to make two locations without the use of the third point. This is done by setting up in line with and orienting by sighting to them as before. A range line is drawn on the board through the two points and a point assumed on this line from which a foresight is drawn to an object in sight of the located points. A signal is erected at the occupied point and the newly sighted object gone to. On arriving at the new station orient by sighting back to the signal just left. The table is now in correct position parallel to that when on the range line. The location of the point will be the intersection of the two lines drawn from the located points. Now, putting the alidade over this point and sighting at the signal we may locate it by intersecting the range line.

It is seldom that the circumstances will be such that the above method can be used, but even if they are, only two point locations will be obtained and considerable time spent.

Locations are also made by what is known (ref. 7 and 9) as the *three point method* and it is sometimes desirable to use it in the following cases: (1) When several or all of the triangulation stations are inaccessible; (2) when it is found that a mistake has been made in identifying a foresight, in which event it is desirable to avoid loss of time required to go back to the original station to

verify it; (3) to save time in erecting signals; (4) on account of poor paper, inaccurate projection of sheet or points on it, poor telescope, or imperfectly drawn lines, so that the intersections or resections do not pass through a common point.



In the diagram shown above the triangle formed by the three fixed points is called the *Great Triangle*, and the circle passing through them the *Great Circle*.

In case the table is *imperfectly* oriented, the lines drawn from the fixed points will not intercept at one point, except as is shown in Case 3, but will form a *triangle of error*.

Case 1.—When the new point is within the great triangle, the point sought is within the triangle of error.

Case 2.—When the new point is within either of the three segments of the great circle formed by the sides of the great triangle, orient on the middle point; then the line from the middle point lies between the true point and the point of intersection of the lines from the other two points.

Case 3.—When the new point is on or near the great circle, *the location is uncertain.*

Case 4.—When the new point is without the great circle, orient on the most distant point; then the point sought is always on the same side of the line from the most distant point as the point of intersection of the other two lines.

The new point is *always* on the same side of each line drawn from the three fixed points, that is, if it is on the right side of one line it is on the right side of each of the others; if on the left of one, it is on the left of the others.

The true point is *always* distant from the three lines drawn from the three fixed points, in direct proportion to the distance of the three points from the point occupied.

Since a location can be made from any three points, whether correctly plotted or not, the *location should always* be *checked* by a *fourth point* if possible.

When the true point has been estimated and lightly marked on the sheet with a pencil, the triangle should be erased, and a new orientation made. If the lines from the three fixed points now intersect at that point, the position is determined. If a new triangle is formed, the operation must be repeated.

In making three point stations, the compass will be found convenient to give approximate orientation.

Bessel's method by inscribed quadrilateral is a simple method of construction but is objectional in practice because the intersection of the lines of construction often fall beyond the limit of the board (ref. 9).

Another method consists in laying off the angles between three known points on tracing cloth or paper and using this as a protractor to determine the position of the unknown point.

This is done by fastening a sheet of tracing cloth or paper to the board and taking any point on it as the unknown point. From this point lines are drawn toward the three unknown points. The cloth or paper is then shifted over the sheet until each of the three lines passes through the plotted point corresponding to the point toward which it is drawn. The position of the unknown point is the assumed point on the tracing cloth.

This method is less exact and not as convenient as the first one given and is impracticable in any wind. The cloth or paper is liable to get rumpled and unfit for use unless great care is taken.

Three point stations should never be used to work out from, except in case of absolute necessity, as is the case when all the primaries are inaccessible.

Road junctions or crossings form the best possible control points and are always located whenever possible. They not only hold the road traverse, but, since levels are run over all the roads and elevations are always obtained for these points, they give base levels from which plane table elevations may be worked out. The location may be obtained by any of the methods already given and the azimuths of the road shown. It may often happen that while a

station cannot at first be made in the road itself, it is possible to make a location at some nearby point. When this is done the center of the road is obtained by sighting and measuring to it. Orientation good enough to show the azimuths of the roads may be obtained by sighting back at a small piece of paper placed on a stick to the rear of the first location in line with the shot to the road.

The whole sheet is safest and usually best controlled by means of foresights, locations being made by intersections or resections from the primary triangulation stations or the most accurately located point.

After the field work is finished the points are inked in. Care is taken to erase no lines on the sheet. The following symbols are generally used to show the character of the point.

for primary triangulation stations (red ink).

for secondary triangulation stations.

for secondary triangulation stations (flag signal).

for secondary triangulation stations (tree signal).

for secondary triangulation stations (flag in tree).

for located houses or barns.

for located schoolhouses.

for located churches.

for located windmills.

for located chimneys or standpipes.

for located deciduous trees.

for located pine or fir trees.

for located dead trees.

for located hill tops, spurs, etc.

for located water tank.

for located oil derrick.

for located cemetery.

The number and sometimes a short description is given. Also the names of the primaries and most prominent places.

All that remains is to work out the elevations of the points to which angles have been taken. This is usually done on rainy days during the work. The angles are obtained directly from the notes and the distances scaled from the sheet. By the use of tables compiled directly for this work we may obtain the difference of elevation (ref. 7). As the control is generally a month or so ahead of the rest of the work, this is all that can be done at this time. At least two wye level elevations, say one in the north and one in the south portions of the sheet, must be given. A description of the points, whose elevations are required, are given to the level man and as soon as the levels are run he will report them to the triangulator, who can then finish his work. By adjusting the different elevations obtained for each point, giving each a weight according to its value, very good results are obtained. The two level points are selected primarily on account of the number of angles taken from or to them, but if possible, they are chosen so as to be easily assessible to the level men, that is, near a highway. If any stations have been made in or very near the roads, they are also given.

In laying out the work the question of *cost* must always be borne in mind. This means, not only the living and transportation expenses and price of materials, but also the saving of time.

As the greater part of the work of the plane tableman is on private property, considerable time may be spent in explaining the work to the owners. This, however, is one of the duties of the triangulator and should be treated as such. It is not only due to the owners, but is in accordance with orders to show courtesy to the public while engaged in official duties and to take time to answer any serious inquiries concerning the work of the survey. Much of this time may be saved by giving an account of the work, with especial reference to local conditions, to the newspapers, and referring all persons to them. In case no papers are published on the sheet, the country store keeper or doctor will be found to be an excellent substitute. Such news often travels rapidly, especially in country districts, and many persons become interested and often greatly aid the work. Many arguments may be saved with people who are personally hard to convince, but who will believe anything published in a local paper or retailed from the country store.

While the members of the survey are not ordered to wear the survey uniform, it is *earnestly requested* that they do so. It will be found advisable to wear it not only on that account, but also on account of its strength and cheapness, and better still, because it often prevents doubt in the mind of a land owner as to the surveyor's statement that he is on private property for the purpose of doing government work.

Rates are obtained at hotels and liveries when possible. By informing the proprietors that other parties on the same work are following, and that a recommendation will influence their actions, better service is generally obtained.

Signal cloth is bought in quantities and considerable reduction so obtained.

It may occur that time may be saved by taking either train or trolley to some other town and there hiring a rig rather than driving out and back. The cost of such transportation, together with the cost of the team, and the effect this will have on the rate of the regular liveryman, beside the saving of time, must be considered. The same effect as to hotel rates will apply, if it is desirable to remain away from headquarters for a few days. When staying out

overnight with a team, it must be remembered that feed must be purchased and that in case of rain on the following day, not only must the feed be paid for, but also the team, which would not be used, had the headquarters been returned to.

While it is usually necessary to use two horses, there may be days in which one can be used to equal advantage.

When the assistant has obtained a little experience he may be allowed to do some of the flagging by himself and so save considerable time.

In the South, government stock and outfits are used almost entirely, the greater part of the men living in camp. As the plane table work is generally done ahead of the rest, or even if started at

U. S. G. S. Camp, Bristol, Harrison County, W. Va.

U. S. Geological Survey Camp on Cherry Camp Run, near Bristol, W. Va. April, 1903.

Oil rig showing in background.

the same time, moves with twice the rapidity, the triangulator will live on the country during most of the work.

In many places the scarcity and poor condition of the roads will prevent his working out of one place for the whole sheet. Under such conditions it is seldom that any great reduction can be obtained in hotel rates so that it is advantageous to be away from

the headquarters for several days at a time, putting up wherever the day's work happens to end.

Breakdowns often occur on the road, but wheels braced with hickory or white oak saplings and hickory poles or singletrees will often last for some time and allow permanent repairs to be delayed until a rainy day.

A 15-minute sheet is usually controlled in from three to six weeks, depending on the character of the country and the weather. A timbered sheet will probably take three weeks to flag and one to control, while a sheet in highly developed country may require but one week's flagging and three with the instrument, allowing four weeks to each sheet, which would be good time with fair weather on a sheet well controlled with primaries.

Primary Traverse (ref. 1, 5 and 6).

In heavily wooded and level country or on the prairies of the Central West it is often found to be inexpedient, because of great expense, to procure control by means of triangulation. Under such conditions it is obtained by what is known as *Primary Traverse.* It is also found advisable to use this method in country which has been covered by primary triangulation but where the points obtained are on flat tops or the sides of hills away from the work, so that secondary triangulation is impossible without going to considerable expense.

The instruments used are: a good transit, reading to 20 or 30 seconds; a 300 foot steel tape, graduated to feet for 5 feet at either end; a 100-foot steel tape; a spring balance; two thermometers, four hand recorders; two flag poles, and a good watch.

The party is made up of a transitman, a recorder, two tapemen, and a flagman.

The work consists in running traverse lines of high degree of accuracy by means of transit and tape over railroads or highways in such a manner as to give the required control.

A record is made giving a description of the starting point of the line, and the beginning and ending of each day's work; also locations of railway stations, mile posts, and switches passed; and roads, streams, and town, county and state lines, crossed. Two permanent marks such as are used on primary triangulation stations are placed not less than 500 feet apart at the initial and terminal points. The tape is used at 20 pounds tension and the

temperature taken every hour during the work. Polaris observations are taken every night, when possible, and at distances of not more than 10 miles. When the line is very crooked, solar azimuths are taken twice a day, weather permitting, in addition to the Polaris observations.

The effect of errors is practically eliminated by closing the traverse back on itself, or on some other adjusted primary traverse, or, better still, by connecting with primary triangulation stations or astronomical positions.

The latitute and longitude of all determined positions are afterwards computed.

SPIRIT LEVELS (ref. 1, 5 and 6):

In order that the contours of the finished maps may show exact elevations above sea level, part of the topographic work consists in running a system of spirit levels over the country to be worked.

A sufficient amount of accurate leveling is done to place at least two permanent bench marks in each township or equivalent area, except in forest clad or mountainous countries, where but one is established. In addition to these, other bench marks are located in prominent places, where they may be of service in the prosecution of future public or private surveys.

For each general locality of field work some centrally situated place is chosen in which the elevation above sea level can be determined with approximate accuracy from railroad or other surveys. In this place are established two central datum bench marks, preferably tablets cemented in some solid masonary structure, to which will be referred all other bench marks in its neighborhood. Bench marks consist of circular bronze or aluminum tablets, 3½ inches in diameter and ¼ inch thick with 3 inch stems, fastened with Portland cement into solid rock or masonary structures, as the foundation of buildings or bridge piers, or of 3½-inch bronzed-capped wrought iron posts, 4 feet long, split at the bottom and expanded 12 inches, so as to prevent both their settling, or being pulled from the ground. The latter are set on a flat rock, if possible, and so as to project one foot above the surface. They are set so that they will not be liable to injury or disturbance, yet prominently situated, so that they may be easily found.

Datums are established and all neighboring benches based on their elevations, in order that topographic work may proceed with-

out having to wait until different lines of precise levels are carried into the country to be worked.

In order that the bench marks may be marked to satisfy the scientific demand for exact differences between them and also the popular demand for approximate sea level heights, they are not given serial numbers, but are stamped with the elevation above mean sea level to the nearest foot, as determined at the time of running the levels, and, in addition, with an abbreviation of the name of the central datum point. The more exact, accepted elevations are changed whenever new determinations of the datums are made and may always be obtained from the Survey office in Washington.

PRECISE LEVELS are run by a party consisting of a levelman, two rodmen, an umbrella man who also acts as bubble tender, and a laborer.

The instruments consist of a level, having a 4-second bubble; two rods of special design, 10 feet long, nonextensible, made of selected white pine, and treated with boiling paraffin or linseed oil; and four steel turning points 12 inches long.

The line is a double-rodded one, and the four turning points are all used at the same time, two for each rodman. They are used that those employed for back sights are not withdrawn until the foresight pegs have been set, so that the line, at no time, depends on the stability of the level. The instrument is always shaded from wind and sun, fore and back sights are of exactly equal lengths, and no sight over 300 feet in length is permitted except in special cases, such as crossing a stream. The limit of apparent error, in feet, is fixed at $.03\sqrt{\text{distance in miles}}$.

The PRIMARY LEVELS are run by a levelman and one rodman. The instruments are 20-inch engineers' levels with 10-second bubbles. New York rods, having a special foot-plate made of a truncated pyramid of brass, the bottom of which is but one half inch in width, are used. Plumbing levels are carried to keep the rod verticle. Turning points are taken on steel pins driven firmly in the ground. Except when crossing streams, fore and back sights are not taken over 300 feet and, when possible, are of equal length. When it is impractiable to take equal length sights, enough unequal sights are taken to balance the set, as soon as the obstacle is passed. Distance is obtained by counting rails on railroads or by stadia and pacing. Levelmen and rodmen keep separate notes.

When passing, the former reads the rod himself, records, computes, and compares resultant elevations or H. Is. with the later.

The lines are run over the railroads or most level highways so as to give sufficient control for flying levels and to form, where possible, either a closed circuit or one joining some other line.

Besides the permanent bench marks, temporary ones are left about every mile and at the end of the day's work. They may be chiseled on a solid rock, or a nail may be driven in a knuckle cut on the root of a tree. Elevations in the center of the road are taken at crossings of highways, railroads, summits, streams, bridges, and in front of railway stations and public buildings, when passed. They are painted in large figures, with the prefix U. S., to the nearest foot, in some conspicuous place such as on a fence or side of a barn.

The allowable error, in feet, for this work is

$$.05 \sqrt{\text{distance in miles.}}$$

FLYING LEVELS are run over all the roads not covered by the primary line by a levelman and rodman using an ordinary level with a 20-second bubble. New York rods with 4-foot extensions are used.

Lines are started from primary elevations and closed on them as often as possible. The rod is read to the nearest .01 and sometimes .1 of a foot and turning points taken on any solid substance at hand.

Elevations are obtained for the same places as was done by the primary men and marked in the same manner.

When required, flying levels are run to plane table points.

ROAD TRAVERSE (ref. 5, 6, 10).

After the plane table triangulation or primary traverse has been completed and after or at the same time as the leveling, the roads are travesed. This work is done by one man using a small, 15-inch, square plane table, having a 3 inch box compass inserted in one edge of the board. The alidade is a brass rule, 6 inches long, graduated to a scale of 1 in 45,000 and 1 in 90,000, and having hinged sights which fold close to the ruler.

Before starting in his work, he is given a sheet of paper, similar to that used on the large plane table, but of lighter grade, on which has been placed approximately the control points with reference to the magnetic declination for a one quarter sheet. He also measures, to the nearest .1 of a foot, the right, forward wheel of a buggy,

which he will use for the work. He will then either make or (ref. 7) obtain a small table converting wheel revolutions into hundredths of a mile or scale divisions.

If possible, he will start his work at some control point, which he can find from the furnished descriptions. Starting at the given or assumed point, he levels his table by eye and sights through his alidade to the first bend of the road to be traversed. Then jumping in his buggy, he drives to the bend, counting his wheel revolutions by means of a piece of cloth or leather fastened to one of the spokes. On arriving there, he dees not stop, but putting down the number of revolutions in his note book, continues driving to the next bend, counting all the while. Here he sets up his table again, orienting by use of the compass and scales off the distance along the line drawn at the former station to the first bend and marks its location by a needle point. Then, using the needle as a pivot, he sights to the bend just located and draws a line along the alidade toward the occupied station. This is also located by scaling the traversed distance and a fore sight taken to the next bend. Stations are made at all road junctions or crossings and the azimuths of the roads shown. Beside this, the number of revolutions is set down each time a house or stream is passed and the points plotted at the following station. A large circuit is usually run at first, and later the interior roads traversed. Due to the rapid and rough methods, notwithstanding the care taken, it is seldom, if ever, that perfect closures are made. These errors are shown by a light curved line joining the two locations of the same point. Closures are never made in towns or villages. After the traverse is completed, as far as the immediate road is concerned, one ach, station, the traversemen will get location of all prominent objects between roads, that will aid in adjusting and sketching, by intersections. Shots are taken to houses at a distance from the road, flags or lone trees on hills, hill tops, spurs and outlines of ponds and woods. These are shown by the same symbols as are used on the palne table sheet. Wood lands are shown by crimpled lines. All small ponds near the roads, aretraversed to and surveyed.

Great care is taken in getting *control points*, not where they have been approximately plotted, but where they are shown to be by the traverseman's intersections. If they cannot be intersected easily they are traversed to, on foot, if necessary. When the streams are near the roads, they are sketched in. When the roads have been

leveled, the elevations painted on the fences, etc., are located and recorded on the traverse sheet. In rough country, with few roads and distant ridges and valleys, the hollows are traversed, on foot, if necessary. While this takes considerable time, it is of great value to the sketcher, and often saves his more valuable time, in doing the same work. State, county, town and district lines are obtained, and also names of towns, streams, hills, etc., and recorded on the sheet. When working, all the sheet, except that in immediate use, is covered with paper, small openings being made as required. A piece of paper is also pasted on the bottom of the alidade.

SKETCHING (ref. 6).

The final and last stage of the field work to which all the others lead up to is the sketching. This requires the greatest skill and experience and is generally done by the topographer in charge of the work.

The sketch sheet is a piece of paper of the same grade as that used in the plane table triangulation, but of one half the size, as a full sheet is too cumbersome to handle conveniently. It has plotted on it the primary and secondary control points, the road traverse adjusted between these points, so as to eliminate all closure errors, and the elevations from vertical angulation or spirit leveling written in their appropriate places.

The topographer is equipped with a Johnson tripod and plane table board to fit the sketch sheet, a small telescopic alidade, a hand level, a clinometer, and an aneroid barometer.

In open country where roads are sufficiently abundant to cut up themap with traverses so near one to the other that the topographer may not have to sketch more than one half to one inch to either side of his position the work proceeds as follows:

Taking the sketch sheet on the board in his lap, the topographer for cheapness and convenience, because of the speed, drives over every road. Where these are not sufficiently near, he walks in between them, pacing distance as a check, and better locating himself, when possible, by resections from fixed objects, while he sketches the plan of the contour lines as far as he can safely see them to either side of his path. This operation is performed by setting out from such fixed points as a road junction, a located house, or a stream crossing, the position of which is plotted on his map and the elevation of which is known. Adjusting the index of his aneroid at the

known elevation, he drives or walks along, keeping the plotted position of the road parallel to its position on the ground when driving over it, and marking on the map the crossings of contours as shown by the barometer. At every contour interval he stops, and, knowing his position on the map, follows the contour by eye, or by hand level, and sketches it on the sheet. The aneroid is checked every two or three miles either from elevations already given, or by new ones obtained by taking vertical angles to points in sight, whose elevations are known. In this same way he is able to com-

Foot-Traverseman at Work.

Foot-traverseman or "ridge hiker" starting in work near Glenville, Gilmer County, W. Va. Small 15 inch traverse table and sight alidade being used. Lunch carried in haversack and water in canteen. Horse will be tied to a tree, fed, and returned to and ridden in at night.

pute the elevations of nearby hilltops or spurs, which either he or his traverseman has located by intersections so as to aid in accurately placing the contours. He not only sketches the contours, drainage, political boundaries, and other topographical features in the assigned area, but also checks the positions of houses, summits, streams, etc., as located by the traversemen.

When the hills are more prominent and the slopes bolder and steeper, the topographer sketches these from his various view points by interpolating contours between located control points.

In the woods the sketching is executed in an entirely different manner. The topographer is limited to sketching that which is directly under foot, or, in other words, mere contour crossings. Not only the topographer, but his more skilled assistants are engaged in this work. Foot traverse is run along the stream beds and ridges and the contour crossings obtained. This work is done on small plane tables with sight alidades. Distance is obtained by pacing or by use of a light linen tape. When the skeleton of topography on the highest and lowest lines, *i. e.*, contour crossings of streams and ridges, is plotted on his map, the topographer readily interpolates contours for most of the intermediate spaces and, following his assistants, fills in those places which are not fully mapped.

The maps are inked in the office; photographed, and, at the same time, reduced to the published scale; engraved on copper; and printed.

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THE TREATMENT OF COPPER ROCK AT THE QUINCY MILLS, HUBBELL, MICH.

By C. K. HITCHCOCK, JR., E.M.

The rock treated at the Quincy Mills is a moderately hard amygdaloid, coming from the Quincy Mine which is working upon the Pewabic Lode. It contains, at present, about 1¼ per cent. of native copper and varying amounts of quartz, calcite, epidote and the zeolites filling the amygdules. Since the specific gravity of the copper is far in excess of any of the other constituents of the rock, it will be seen that the difficulties in milling arise more from the low grade of the rock than from the nature of the separation. As is the case in all low grade milling operations, a fraction of a per cent. of the valuable mineral, more or less, in the tailings represents a relatively large variation in the amount saved compared with the original amount in the rock, and of course means much in the profits of the operation.

During recent years efforts have been made to reduce, as far as practicable, the loss in the tailings. Without going into details concerning the experiments and tests in this line, the method of treatment will be described as it is to-day. It will suffice to say that the efforts to reduce the loss in the tailings have been made chiefly in three directions: (1) In obtaining the most economical machines for treating the material; (2) in re-treating material heretofore sent to waste; (3) in making the tailings poorer by increasing the amount of the heads, thereby decreasing the richness of the same. After experimenting for several years, the result at present is: the substitution of Wilfley and, still better, New Standard tables for the old two-deck revolving round tables; the separation, grinding, and further treatment of a middle product from the roughing jigs; and the increasing of the amount of slime copper (No. 3 grade), at the expense of its richness, to a point where the increased smelter charges offset the saving of copper. Beside these, of course, changes of detail in treating the material have been made. The saving of float copper, however, still remains to be effected. The float copper is not due, as in the case of friable ores, to the crushing operations so much as to the shape of the piece. It does not matter so much how small the particle

so long as it is comparatively thick and compact. But the copper occurs in the mine in many places in thin sheets much like foil, and this, when broken up small, will float off in the wash water, in spite of all care taken. The production of fine copper in stamping, however, has been greatly reduced by introducing a mortar discharge, by means of which copper which has been freed from rock, and which is too large to pass through the mortar screens, is taken directly from the mortar while stamping continues. Formerly, this copper remained in the mortar, subject to the stamping which it could not escape. Frequent shutting-down of the stamp-head was then necessary to allow for cleaning the mortar, which is now greatly reduced, resulting in a saving of time. Improved facilities for shipping the mineral to the smelter might be added to complete the list.

The mills, of which there are two, are situated on the shore of Torch Lake, in Houghton County, Michigan. The older, or No. 1 Mill, contains five stamp-heads, and the new one, No. 2, contains three. Although the treatment in No. 2 Mill in particular is described here, the method used in No. 1 differs only in minor details. No. 2 Mill measures 217 ft. by 132 ft. in size, of steel frame, and is situated on a side hill, so that nearly all material is handled by gravity. The storage bins extend the entire length of the building and are 22 ft. wide and 26 ft. deep at the front, holding when full about 2,000 tons. The bottom was constructed by filling in poor rock till it took the natural slope from the back to the front, and by then laying a plank covering over this filling. The foundations of the stamp-heads are built up of concrete and timber from the rock foundation. Power is furnished by a 16 in. by 36 in. engine. Water is supplied at the rate of 16,000,000 gals. per 24 hrs., by a vertical, triple-expansion pump of E. P. Allis make, and is maintained at a constant head by pumping it into an open iron supply tank, provided with an overflow. Formerly, the water was furnished to each mill by a separate pump, but now the two systems are connected so that a break-down of either pump will not necessitate a shut-down of either mill.

The copper rock, having passed through 4 in. grizzlies or through 10 in. by 20 in. jaw crushers at the mine, is dumped directly into the bins from the railroad cars. About 3,350 tons per day are treated by the mills, which represents the output of the mine exclusive of such masses of copper as are cut up underground and

such smaller masses as may be easily cleaned in the rockhouses at the mine. The rock then is fed from the bins to the stamps by means of a chute. These stamps were all furnished by the E. P. Allis Co., but a Nordberg mortar has been substituted for the third head in No. 2 Mill. They make 100 strokes per minute, at 120 lbs. steam pressure. At present, each head is stamping over 500 tons of rock per 24 hrs., which is crushed till it will pass through the five-eighths inch mortar screens. Such pieces of copper, however, as cannot be reduced sufficiently in size to pass through the screens are, from time to time, removed directly from the mortar by means of the mortar discharge. This is done merely by allowing the pieces of copper to pass through an opening in the mortar against a stream of incoming water strong enough to prevent the discharge of the smaller pieces of rock. The copper thus obtained is called No. 1 grade of mineral. Such material as does pass through the screens is conducted over a hydraulic classifier, which consists of a square box attached to the launder in such a way that the material must pass over a strong rising current of water. Whatever is heavy enough to pass down through the classifier against the stream of water is also collected as No. 1 mineral. The other portion passes into trommels and those pieces which are too large to pass through the trommels — that is over one fourth inch diameter — are returned to the stamp by means of a bucket elevator, to be crushed finer. These trommels are of perforated sheet iron with one fourth inch holes, and are 5 ft. 10 in. long by 2 ft. 3 in. diameter at the small end and 3 ft. 5 in. at the large end. They make 15 revolutions per minute. The material passing through the trommels is conducted over other hydraulic classifiers which separate out, as above described, No. 1 mineral, and allow the remainder to go to the roughing jigs. There are two trommels to each head, and each supplies material to three sets of four jigs each, each jig having two sieves, and each sieve being 2 ft. by 3 ft. in size. The jigs are all run at 133 strokes per minute with a one half inch stroke.

The plant is so arranged that each set of four jigs receives the same grade of material, and the supply to each can be regulated by a gate placed in the launder; but the material treated by the individual jigs of each set is classified by being fed against a rising stream of water, so that the first sieve of the first jig, being 8 mesh, receives the coarsest material; the second sieve, 10 mesh, less

coarse; and so on with the first and second sieves of the second jig, which are respectively of 12 and 14 mesh and receive finer and finer sizes. The third and fourth jigs of each set treat the overflow from the first and second jigs respectively, and the sieve in each case is 2 meshes per linear inch finer than the sieve whose overflow it treats. Whatever does not go to the roughing jigs is considered slime and passes on through an overhead launder to the settling boxes, which feed the slime tables. The tailings of the third and fourth jigs of each set go to the waste sand launder.

A middle product is obtained from both sieves of the third jig of each set, that is, the jig treating the overflow from the jig which receives the coarsest material. This middle product is drawn off through a three-fourths inch pipe entering a little above the sieve, an operation which is accomplished by admitting air through another pipe at this point. This material runs in a launder to a Chilian mill in Mill No. 2, and to a Huntington mill in Mill No. 1, where it is reground and treated as will be described later. As the jigs run with considerable suction, a large amount of hutch work is obtained. This is treated on the finishing jigs and tables.

The finishing department consists of two sets of three two-sieve jigs and two Wilfley tables to each head. These jigs are of the same size as the roughing jigs, but are of a more recent design in that the motion is imparted to the plunger by means of an eccentric instead of the rocker arm, whereby the motion is more easily regulated. They are run at 165 strokes per min., with a three eighths inch stroke. The material coming to each set passes over a hydraulic classifier, the overflow from which feeds the two sieves of the first jig the same as in the case of the roughing jigs. Stuff too fine for treatment on the jigs passes into a settling box whence it is fed to a Wilfley table. The overflow goes to waste. Whatever goes through the hydraulic classifier, together with the hutch work from the first finishing jig of each set, contains all the silver that is saved. Formerly, No 1 mineral was picked over by hand for silver, but this is now found not to pay.

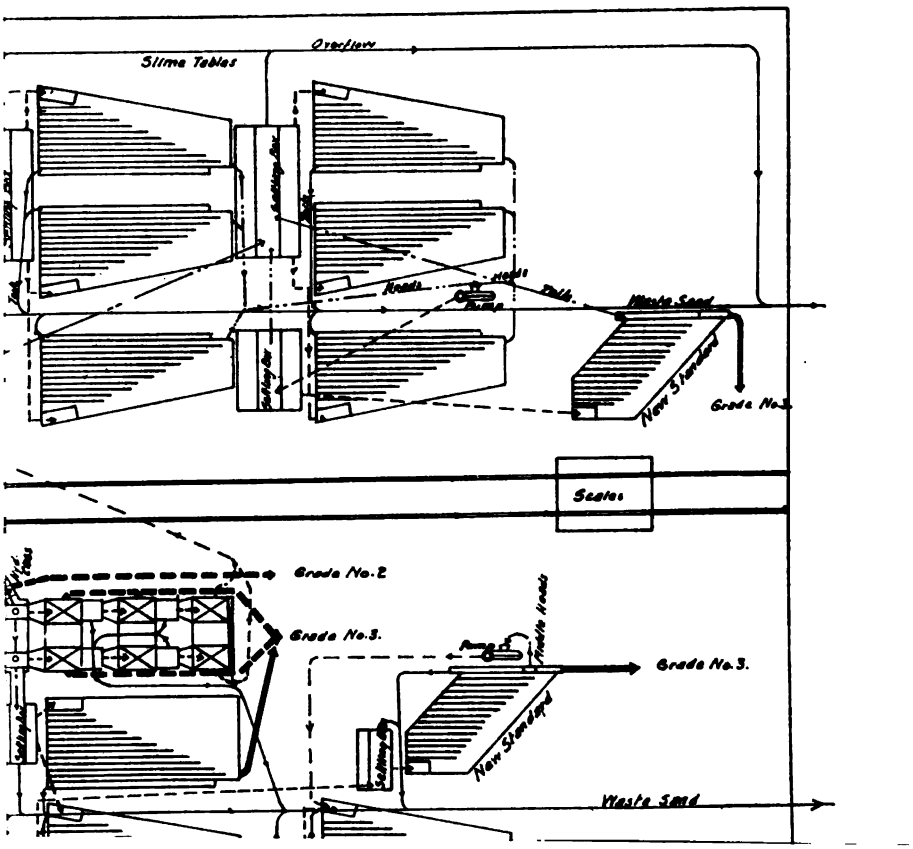
The overflow from the first finishing jig is treated by the second jig and the overflow from this, in turn, is treated by the third jig. The overflow from this last goes to waste. The hutchwork of the second jig is collected in a box and is called "No. 2 mineral." That from the third jig is too poor for a finished product and is retreated on the slime tables. The concentrate from the Wilfley tables mentioned above is called "No. 3 mineral."

The slime department consists of nineteen Wilfley tables, a set of jigs and four "New Standard" tables. The Wilfley tables are of the standard size and treat 25 tons of material a day. The New Standard tables are found to yield a better concentrate and so are used to furnish the finished product, while the Wilfleys discard the tailings. As stated above, the material coming to these tables is stuff that is too light for treatment on the roughing jigs. Before reaching the tables it is received in six settling boxes, two to each stamp-head. These boxes are 11 ft. by 5 ft. 6 in. in size, rectangular in plan but pointed in elevation, with a depth of 3 ft. 9 in. They are elevated about 10 ft. above the floor and the tables are fed by small closed launders. Each settling box feeds three Wilfley tables. The tailings from the tables go to waste, but the heads from each group of six Wilfley tables are collected, and by means of a centrifugal pump are sent to another settling box, from which a New Standard table is fed. The heads from these New Standard tables are collected and are called "No. 3 mineral" or "slime copper." The tailings are returned to one of the first named settling boxes for retreatment on the Wilfleys.

The Chilian Mill mentioned above as treating the middle heads from the roughing jigs, has a six-foot mortar with 10 mesh mortar screens. It is run at 25 revolutions per minute and treats 60 tons of material per day. The crushed material passes from the grinder over a hydraulic classifier to a set of three two-sieve jigs, precisely similar to the finishing jigs.

The product of the classifier is "No. 2 mineral," the hutchwork from the first two jigs is "No. 3 mineral," and the hutchwork from the last jig is retreated on the slime table. The fine overflow passing the jigs is treated on a special Wilfley table, from which the heads are saved.

Until recently the different grades of mineral were packed in separate barrels, as has long been the custom in the Lake Superior region, and shipped to the smelter by rail. This is a primitive and expensive method of shipping mineral where any considerable amount is to be handled, and has now been abolished at the Quincy Mills. The mineral is shipped in bulk in special cars by rail to the smelter, which is situated a short distance east of Hancock, on Portage Lake. The different grades are now collected from the concentrators in a bucket which holds 400 lbs. and which is suspended from a traveller running on a 6 inch I beam


Slime Tables
Overflow
Waste Sand
New Standard
Grade No.3
Scales
Grade No.2
Grade No.3.
Grade No.3.
New Standard
Waste Sand

overhead. The contents of the bucket are emptied into small cars holding from 2½ to 4 tons each, depending on the grade of mineral. The cars enter the mill on the ground floor, where they are filled and made up into trains which are hauled by an electric locomotive — like those used underground at the mine — to the old mill, where the contents are dumped into bins. In the old mill, the collecting bucket empties directly into the bins. These bins are large enough to hold two days' supply and are divided into compartments for the different grades of mineral. The empty mineral cars are brought in and spotted on a 54 ft. set of railroad scales, the compartments of which correspond to the compartments in the bins. Each grade may now be run separately into the cars without any necessary movement of the latter, and at the same time the amount of mineral is weighed directly or by difference. A further advantage is secured over the old barrel method in that there is a greater elimination of moisture before the mineral reaches the smelter. When once the mineral was barrelled it lost but little moisture, and in winter it generally froze so that a great number of barrels were destroyed getting the frozen mineral out. Now the moisture drains while in the bins and in the cars, and is exposed to the cold only while in transit to the smelter. At the smelter, bins have also been constructed, where further drainage takes place, before the mineral is charged to the furnaces.

NOTES ON ORGANIC ANALYSIS. PART IV.

By HENRY C. SHERMAN.

CHAPTER XI.

Butter.

Butter is officially defined* as 'the product made by gathering in any manner the fat of fresh or ripened cream into a mass which also contains a small portion of the other milk constituents, with or without salt.' Standard butter contains not less than 82.5 per cent. of butter fat, having a Reichert-Meissl number not less than 24 and a specific gravity not less than 0.905 at 40°/40°. By acts of Congress approved August 2, 1886, and May 9, 1902, butter may also contain additional coloring matter.

Butter may fail to meet the requirements of the official standard either because of a deficiency in the percentage of fat or because of the presence of foreign fat or butter fat of abnormal character, though the sample may contain nothing which can be regarded as unwholesome. Butter analysis therefore includes (1) the examination of the whole butter, (2) the examination of the butter fat.

This chapter will be devoted mainly to the methods of examining butter fat but for convenience the determination of water, fat, curd, and ash will be described first. The point at which tests for preservatives can conveniently be made will be indicated, but the detection of foreign colors will not be considered as these are not regarded as adulterants.

DETERMINATION OF WATER, FAT, CURD, AND ASH.

Especial care must be taken in sampling butter since the water, salt, and curd are often unevenly distributed and an attempt to mix by stirring is apt to result in squeezing out drops of brine. If a large quantity is to be sampled a butter trier should be used, and the portions thus drawn united until a working sample of about 500 grams is obtained.

Melt the sample at the lowest possible temperature in a wide-mouthed glass-stoppered bottle, shake violently to ensure a homo-

* Circular No. 13, Office of the Secretary, U. S. Dept. Agriculture.

geneous mixture and continue the shaking while cooling the sample until it is sufficiently solidified to prevent any separation of water and fat.

Thoroughly clean and dry a lipped dish or beaker having a flat bottom of at least 20 square centimeters. Weigh the dish, introduce 1.5 to 2 grams of butter and re-weigh quickly to avoid evaporation. Dry to constant weight in a boiling water oven. The loss is *water.* Treat the dry residue with petroleum ether or benzine, transfer it to a weighed Gooch crucible having a felt of ignited asbestos and wash with the solvent until all fat is removed. Dry the crucible and residue to constant weight in a water oven or an air bath not above 110°. The material dissolved by the petroleum ether or benzine is *fat.* Burn the *curd* at a temperature below a red heat and weigh the crucible containing the *ash.*

Notes.— The method given is essentially that of the Association of Official Agricultural Chemists.* If preferred the butter can be dried on clean dry sand or asbestos. When the latter is not used it is important that the butter form only a very thin layer on the bottom of the dish or beaker; otherwise the water sinks into the melted fat and is only very slowly expelled at the temperature of the boiling water oven. For convenience in transferring and washing the residue with petroleum ether the latter should be used in a small wash bottle having a ground glass stopper. Instead of drying in a dish and transferring the residue to a crucible, the butter may be weighed directly in a crucible two-thirds filled with fibrous asbestos, dried to constant weight and then extracted.† A device for facilitating this drying by passing a current of air through the heated crucible has recently been described by Bird.‡

Great care must be taken to burn the curd at the lowest temperature possible in order to avoid loss of chlorine (see Chapter I.). Any small amount of milk sugar which the butter might contain would be counted as curd in this analysis. The percentage of salt can be found by determining chlorine in the ash, or by repeatedly washing the butter with hot water in a separatory funnel and titrating the combined washings with a standard solution of silver nitrate. Good butter usually contains 10 to 14 per cent. water, 84 to 87 per cent. fat, 0.5 to 1.5 per cent. curd, 2.0 to

* Bul. 46, Bur. Chem., U. S. Dept. Agriculture.

† Richards and Woodman: Air, Water, and Food (2d Ed.), p. 201.

‡ *Journ. Amer. Chem. Soc.*, 1905, 27, 818.

4.0 per cent. ash if salted; if unsalted, 0.25 to 0.5 per cent. The water content of butter has often been limited by legal or trade standards to 16 per cent. This is considerably above the present average for creamery butter, as shown by an investigation made by the United States Department of Agriculture in 1902.* Of 800 samples from 400 creameries in 18 states, the average water content was 11.78 per cent.; 85 per cent. of the samples contained between 10 and 14 per cent.; the extreme limits were 7.20 and 17.62 per cent. The amount of salt added to butter varies greatly with the demands of different markets, but over 5 per cent. would be excessive unless the butter were intended for export to a tropical country. An excessive amount of curd indicates careless manufacture or fraudulent increase of weight and is likely to injure the keeping qualities of the butter.

EXAMINATION OF BUTTER FAT.

PREPARATION.

Melt 100 grams or more of the butter and allow it to stand at 45° to 55° until the water and salt settle to the bottom.† Pour off the melted fat by decantation and filter it through a dry paper in a funnel heated by a water jacket or supported in a drying oven kept at about 60°. The filtered fat, which must be free from turbidity, is received in a wide-mouthed bottle and kept stoppered in a cool place until analyzed.

REICHERT-MEISSL OR REICHERT-WOLLNY NUMBER.‡

This number is a comparative measure of the proportion of volatile acids, and is the most important basis for deciding the purity of butter fat. Often the presence or absence of foreign fat in butter, or the proportion of butter fat in oleomargarine, is inferred from this number alone. In the interest of uniformity of results official chem-

* Circular No. 39, Bureau of Animal Industry; *Analyst*, 1903, 28, 184.

† This water solution can be tested for preservatives, of which boric acid and borax are most likely to be found in butter. For methods see the chapter on milk analysis, or for more detailed directions Leach's Food Inspection and Analysis, or Lewkowitsch's Oils, Fats, and Waxes.

‡ Reichert: *Ztschr. anal. Chem.*, 1879, 18, 69.

Meissl: *Dingler's Polytech. Journ.*, 1879, 233, 229.

Wollny: *Milch Ztg.*, 1887, 16, 609; *Analyst*, 1887, 12, 203, 235; 1888, 13, 8, 38.

These papers are reprinted in Ephraim's Original Arbeiten über Analyse der Nahrungsmittel.

ists have sought to describe the method in such detail as to eliminate variations due to manipulation.

Reagents. — 1. Caustic soda solution, made by dissolving sodium hydroxide (nearly free from carbonate) in an equal weight of distilled water.

2. Alcohol, 92 to 95 per cent., containing no appreciable amount of volatile acid, either free or combined.

3. Dilute sulphuric acid, made by mixing pure concentrated sulphuric acid with four times its volume of water.

4. An accurately standardized approximately tenth normal solution of barium (or sodium) hydroxide.

5. A 1 per cent. solution of phenolphthalein in alcohol.

Determination. — Thoroughly clean and dry a flask of 250 to 300 c.c. capacity. Weigh the flask, thoroughly mix the melted fat, introduce 5.6 to 5.8 c.c. measured at about 50°, allow the flask and fat to cool for 15 to 20 minutes and re-weigh (or, if convenient, weigh exactly 5 grams of fat into the flask). Add 10 c.c. of the alcohol and 2 c.c. of the caustic soda solution, attach the flask to a reflux condenser and boil on a water bath or electric heater for at least half an hour to ensure complete saponification.*

Evaporate the alcohol by heating the flask in a steam bath, shaking occasionally to avoid danger of loss from frothing and to facilitate the removal of the alcohol. Add 132 c.c. of recently boiled distilled water, warm at 60° to 70° until the soap is completely dissolved, add 8 c.c. of the dilute sulphuric acid and a few pieces of pumice stone, re stopper the flask or connect it with a condenser and warm without boiling until the fatty acids separate as a clear layer. Distil through a glass condenser, collecting the distillate in a flask accurately graduated at 110 c.c. The distillation should be so regulated that 110 c.c. will be collected in from 28 to 32 minutes. Mix the distillate, filter through dry paper, and titrate 100 c.c. of the filtrate, using 0.5 c.c. of the phenolphthalein solution as indicator, until the red color remains apparently unchanged for 2 minutes. Increase the burette reading by one tenth (on account of the 10 c.c. of distillate not titrated), and calculate the number of cubic centimeters of tenth-normal alkali which would have been required if exactly five grams of fat were taken for the determination. This is the Reichert-Meissl number.

*The saponification can also be accomplished by heating in a closed flask, using either aqueous or alcoholic alkali, or by means of the glycerol-soda solution proposed by Leffmann and Beam: *Analyst*, 1891, 16, 153.

Notes.—The number thus found does not represent the total volatile acids present. The yield is fairly uniform if the given conditions of dilution and distillation are maintained. Wollny submitted this method to an exhaustive examination and pointed out the following sources of error: (1) absorption of carbon dioxide during saponification, (2) formation of esters during saponification, (3) formation of esters during distillation, (4) coherence of fatty acids during distillation resulting in holding back some of the volatile acid, (5) variations in the proportion of volatile acid carried over, due to differences in size and shape of distillation apparatus. In order to avoid discrepancies from these and other causes he published an elaborately detailed system of manipulation and precautions. It has been shown that Wollny greatly overestimated the probable errors of the method as previously carried out and that some of his precautions are unnecessary, but as in the main they tend toward greater uniformity of results, they have been adopted with slight modifications by the Association of Official Agricultural Chemists, whose methods * are usually accepted as standard in the United States and should be followed exactly in any determination which is likely to be made the basis of legal action.

In Great Britain, a joint committee representing the Government Laboratory and the Society of Public Analysts has adopted the method essentially as described above with the following specifications for the apparatus to be employed: † Flask used for saponification and distillation; capacity, 300 c.c.; length of neck, 7 to 8 cm.; width of neck, 2 cm. The flask is connected with the condenser by means of a bent glass tube 7 mm. wide, so placed that the bend is 15 cm. above the top of the cork. At a distance of 5 cm. above the cork is a bulb 5 cm. in diameter. The flask is supported on a circular piece of asbestos 12 cm. in diameter, having a hole 5 cm. in diameter in the center, so that the bottom of the flask is heated by a free flame during the distillation. The British committee further prescribed that blank determinations be made and the volume of alkali found necessary to neutralize the distillate (which volume should not exceed 0.3 c.c.) be deducted in calculating the results of each determination. The number so obtained is called the Reichert-Wollny number.

The Reichert-Meissl or Reichert-Wollny number of butter fat is

* Bul. 46, Bur. Chem., U. S. Dept. Agriculture.

† *Analyst*, 1900, 25, 309.

usually between 24 and 34; that of cocoanut fat, between 6 and 8; of other edible fats and oils, usually less than 1.

Specific Gravity.

The specific gravity of butter fat has often been determined either at 100° or at 37.8° (100° F.). The standard recently established for the United States prescribes a minimum specific gravity at 40°, water at the same temperature being taken as unity. Either a specific gravity flask or an Ostwald pyknometer can be used conveniently for the determination, the pyknometer being filled and adjusted while surrounded by water kept at the required temperature, then removed from the water bath, wiped dry on the outside, allowed to cool to the temperature of the balance and weighed.

Saponification Number.

This is determined as described in Chapter IX. Since the normal saponification numbers of butter fat are only about 15 per cent. in excess of those of the fats commonly used as adulterants, the determination in order to be of much value must be very accurately made.

Insoluble Fatty Acids — Hehner Number.

Reagents. — 1. The alcoholic potash solution used in the determination of the saponification number.

2. Alcohol, about 95 per cent. by volume, which leaves no appreciable residue upon evaporation.

Determination. — Saponify 4 grams of butter fat with 50 c.c. of the alcoholic potash solution, evaporate to a paste to expel alcohol, dissolve the soap in about 400 c.c. of hot water in a weighed beaker, add hydrochloric acid in excess of the amount required to neutralize the potash used, and heat nearly to boiling with occasional stirring until the fatty acids have collected in a clear layer on the surface. Cool thoroughly, pour the solution through a filter and wash the cake with cold water without removing it from the beaker. Stir up the fatty acids in the beaker with another portion of hot water (200 to 300 c.c.), cool thoroughly, filter, and wash again. Repeat this treatment three times. After a final thorough washing with cold water, put the beaker containing the fatty acids beneath the funnel and dissolve any fatty acids which the filter may contain by washing with hot 95 per cent. alcohol, allowing the washings to run into the beaker. Evaporate off the alcohol and

dry the beaker containing the fatty acids to constant weight in a boiling water oven.

Notes. — This is the modification of Hehner's method adopted by the Association of Official Agricultural Chemists * and by the chemists of the Government Laboratory, London.† The original method ‡ which is still largely used involves washing the melted fatty acids with hot water on a paper filter. The results thus obtained are usually 1 to 2 per cent. lower than those by the official method. In the hot filtration method there is danger of washing some of the melted fatty acid through the paper.

Iodine Number.

The determination of the iodine number has been fully described in Chapter IX. As butter fat absorbs only 26 to 38 per cent. of its weight of iodine, a gram of sample can be used for each determination. According to Patrick § butter fat shows iodine numbers about 1 unit higher by the Hanus than by the Hübl method.

Melting Point — Wiley's Method.‖

Apparatus and Reagents. — 1. An accurate thermometer reading to 0.1 degree.

2. A tall beaker nearly filled with water and arranged to be heated gradually with constant stirring from bottom to top.

3. A wide test tube suspended in the water in the beaker and nearly filled with water and alcohol as follows: Half fill the tube with hot recently boiled distilled water, then pour a nearly equal volume of hot recently boiled alcohol into the tube, carefully floating the alcohol on the water with as little mixing of the liquids as possible.

Determination. — Allow a drop of the melted butter fat to fall upon a smooth piece of ice floating in recently boiled distilled water. A thin disc of fat about 1 cm. in diameter should be obtained. Remove the disc from the ice by forcing the latter below the water when the fat will come to the surface whence it is

* Bul. 46, Bur. Chem., U. S. Dept. Agriculture.

† Thorpe: *Journ. Chem. Soc.*, 1904, 85, 248.

‡ Hehner and Angell: Butter, its Composition and Adulterations. London, 1874. Hehner: *Ztschr. anal. Chem.*, 1877, 16, 145. Ephraim, *loc. cit.*

§ U. S. Dept. Agriculture, Bur. Chem., Bul. 81, p. 49.

‖ Wiley's Agricultural Analysis, Vol. III.; Bul. 46, Bur. Chem., U. S. Dept. Agriculture.

removed by means of a steel spatula or knife blade and dropped into the tube containing the water and alcohol. The disc sinks to the point where the density of the alcohol-water mixture is equal to its own. It must not touch the side of the tube. Suspend the thermometer so that the bulb hangs in the tube exactly level with the disc of fat. Gradually heat the beaker, keeping the water well stirred. After the disc begins to shrivel, indicating that the temperature is within a few degrees of the melting point, the heat must be applied very carefully. The temperature at which the fat becomes a sphere is taken as the melting point. Repeat the determination twice, heating the bath at such a rate that 8 to 10 minutes are required to raise the temperature through the last 2 degrees. The second and third determinations should agree within 0.2 degree.

Notes.— The special advantage of this method is that it avoids the discrepancies caused by the adherence of the melting fat to solid surfaces, which in most other methods makes it difficult to determine the exact point of fusion. It is important to secure a very thin disc of fat for the determination, to avoid all adherence of air bubbles, and to secure uniform heating of the thermometer bulb and the disc by occasionally swaying the former around the latter as the temperature approaches the melting point. By using hot recently boiled water and alcohol in preparing the test tube for the determination the danger of air bubbles is avoided.

Additional Determinations.

The *index of refraction* and *Crismer's test* * based upon the critical temperature of solution in alcohol are considerably used in the examination of butter fat. They are especially useful where rapid "sorting tests" are required, as in food inspection laboratories where only the suspected samples are submitted to complete examination.

The *phytosteryl acetate test* † is occasionally employed as a means of detecting the presence of vegetable fat, but requires too much

* Crismer: *Bull. Assoc. belge. Chim.*, 1895, 9, 71; 1896, 10, 312; Abs. *Analyst*, 1895, 20, 209; 1897, 22, 71. See also—Weiss: *Pharm. Ztg.*, 41, 268; *Chem. Centrbl.*, 1896, I., 1212. Asboth: *Chem. Ztg.*, 1896, 20, 685. Browne: *Journ. Amer. Chem. Soc.*, 1899, 21, 990. Lewkowitsch: Oils, Fats, and Waxes (3d Ed.), 214, 861.

† Bömer: *Ztschr. Unters. Nahr.-Genussm.*, 1901, 4, 865, 1070; 1902, 5, 1018. Juckenack and Pasternack: *Ibid.*, 1904, 7, 193. Lewkowitsch: *l. c.*, 373.

time and skill for ordinary use and is likely to give misleading results in the hands of an inexperienced person. Cocoanut oil is the only vegetable fat which could be used in any considerable quantity without being shown by the Reichert-Meissl number, and the presence of cocoanut oil is best shown by comparison of the Reichert-Meissl and saponification numbers or determination of the *insoluble volatile acids* as described later.

Acidity of butter fat is sometimes determined and interpreted as a measure of the rancidity, although the odor and taste which cause a butter to be regarded as rancid are more largely due to aldehydes and other decomposition products than to free fatty acids. On the assumption that acidity can serve as a measure of rancidity the term *degree of rancidity* is sometimes used as synonomous with degree of acidity, *i. e.*, to show the number of c.c. of normal alkali required to neutralize the free acid in 100 grams of fat. One "degree" is therefore equivalent to an acid number of 0.56 or to 0.28 per cent. of free oleic acid.

Composition of Butter Fat.

Browne analyzed the mixture of fatty acids from a sample having a rather low iodine number (29.28) with the following results:*

Acids.	Percentage of Acid in Fat.	Corresponding Percentage of Triglyceride.
Oleic	32.50	33.95
Dioxystearic	1.00	1.04
Stearic	1.83	1.91
Palmitic	38.61	40.51
Myristic	9.89	10.44
Lauric	2.57	2.73
Capric	0.32	0.34
Caprylic	0.49	0.53
Caproic	2.09	2.32
Butyric	5.45	6.23
Total	94.75	100.00

This calculation neglects the unsaponifiable matter, which according to Browne amounts to only about 0.1 per cent.

The composition of butter fat is, however, quite variable as will be seen from the range in analytical properties.

**Journ. Amer. Chem. Soc.*, 1899, 21, 823.

VARIATIONS AND RELATIONS OF ANALYTICAL PROPERTIES.

The Reichert-Meissl or Reichert-Wollny number is much the most important of the data obtained in the examination of butter fat. The proportion of volatile acids tends to decrease as the period of lactation advances. The estimated normal range for the other important properties has been given in the table at the end of Chapter IX.

Any of these properties may be influenced by the feeding or health of the animal and occasionally vary much beyond the usually accepted "normal" limits as is shown by the following data collected by Browne.*

	General Limits.	Extreme Limits.
Reichert-Meissl number.....	20–33	11.2[Morse]–41[Nilson]
Saponification number.....	220–236	216[Samelson]–245[Fischer]
Iodine number.....	26–38	19.5[Moore]–49.57 [Farnsteiner and Karsch]

The results of analyses of 357 authentic samples of butter fat collected from various parts of Great Britain and examined at the Government Laboratory, London, have been arranged by Thorpe † according to the Reichert-Wollny numbers and averaged by groups to show the relations between the principal physical and chemical properties of pure butterfat.

The following table shows the averages for each group of samples. The first line, for example, gives the average Reichert-Wollny number for all samples in which this number lay between

RELATION OF PHYSICAL AND CHEMICAL PROPERTIES OF BUTTER FAT (THORPE).

Number of Samples.	Reichert-Wollny Number.	Specific Gravity 37.8° 37.8°	Butyro-Refractometer Reading at 45°.	Saponification Number.	Insoluble Fatty Acids Per Cent.	Mean Molecular Weight of Insoluble Acids.
7	22.5	0.9101	42.0	219.9	90.1	266.9
17	23.5	0.9104	41.5	221.6	89.7	265.5
15	24.5	0.9108	41.5	223.5	89.4	265.0
27	25.5	0.9110	41.3	223.6	89.3	264.2
37	26.5	0.9113	41.0	225.6	88.9	261.9
51	27.5	0.9114	40.6	227.0	88.7	261.7
78	28.8	0.9118	40.1	228.6	88.4	260.9
56	29.5	0.9120	40.1	230.2	88.3	259.6
41	30.5	0.9123	39.9	231.7	87.9	260.1
18	31.3	0.9125	39.7	232.5	87.9	258.0
10	32.6	0.9130	39.4	232.8	87.7	257.8

**Journ. Amer. Chem. Soc.*, 1899, 21, 632.

†*Journ. Chem. Soc.*, 1904, 85, 248.

22.00 and 22.99, with the average of the same samples for each of the other determinations. The second line shows the averages for all samples having Reichert-Wollny numbers from 23.00 to 23.99, etc.

In order to show to what extent increase of volatile acids takes place at the expense of oleic acid, the iodine numbers of 50 of the above samples were determined. Arranging these in groups of 20 and 30 respectively, according to the Reichert-Wollny values, the following average figures were obtained:—

	Reichert-Wollny Number.	Iodine Number.	Oleic Acid Per Cent.	Insoluble Acid Per Cent.	Mean Molecular Weight of Insoluble Acids.
First group,	24.2	40.0	44.4	89.6	264.6
Second group,	30.8	32.4	36.0	88.1	259.8

Detection of Oleomargarine.

Butter substitutes or "artificial butters," unless sold under special names indicating their origin, are collectively termed "oleomargarine" in America or "margarine" in England. The oleomargarine made in America * consists chiefly of refined lard, "oleo oil" (the

* The materials used in the manufacture of oleomargarine in the United States during the fiscal year ending June 30, 1899 (Senate Document No. 168, 57th Congress, 1st Session) were as follows:

Material.	Quantity.	Percentage of the whole.	Value per pound.	Total value.
	Pounds.		*Cents.*	
Neutral lard	31,297,251	34.27	8	$2,503,780.08
Oleo oil	24,491,769	26.82	9	2,144,917.69
Cotton-seed oil	4,357,514	4.77	6	522,025.08
"Butter oil"	4,342,904	4.76	6	260,520.00
Sesame oil	486,310	.53	10	4,863.10
Coloring matter	148,970	.16	20	29,296.00
Sugar	110,164	.12	4	4,406.50
Glycerin	8,963	.01	10	896.30
Stearin	5,890	.007	8	459.60
Glucose	2,550	.003	3	76.50
Milk	14,200,576	15.55	1	142,005.76
Salt	6,773,670	7.42	1	67,726.70
Butter	1,568,319	1.72	20	313,663.80
Cream	3,527,410	3.86	5	176,370.50
Total	91,322,260	100		6,171,007.61

"Butter oil" is commonly stated to be a special brand of cottonseed oil; but the high Federal tax laid upon artificially colored oleomargarine by the law of May 9, 1902, practically prohibits the use of coloring matters employed before that date and has led to the introduction of "butter oils" containing palm oil which is naturally highly colored (Crampton and Simons: *Journ. Amer. Chem. Soc.*, 1905, 27, 270).

soft part of beef fat), and cottonseed oil, often mixed with a small amount of butter and almost always churned with milk or cream. Palm oil and sesame oil are known to be used to some extent and other semi-drying and non-drying oils are probably utilized in some factories.

Hence in comparison with any of the common constituents of oleomargarine, butter fat is characterized by its high proportion of soluble volatile acids, together with a high percentage of lauric, myristic, and palmitic as compared with oleic and stearic acids. The presence of oleomargarine in butter fat, therefore, lowers the Reichert-Meissl and saponification numbers and the specific gravity, while it raises the percentage of insoluble acids and either the melting point or the iodine number or both.

Several European governments require that sesame oil be added to oleomargarine in order to facilitate its detection when mixed with, or substituted for, butter. Similarly the addition of butter to oleomargarine is sometimes forbidden or restricted in order to prevent the production of mixtures too closely resembling genuine butter. The essential features of the oleomargarine laws of the principal countries are given in Lewkowitsch's Oils, Fats, and Waxes.

Detection of Cocoanut Fat.

Since cocoanut fat consists largely of glycerides of saturated acids of low molecular weight, it could be added in considerable quantity to butter fat of average composition without causing the latter to vary beyond the normal limits in any of the important analytical properties. A comparison of the Reichert-Meissl and saponification numbers, however, would lead to the detection of this adulteration since the former number is higher and the latter lower in butter than in cocoanut fat. In pure butter fat the value of the factor [Saponification number — (200+ Reichert-Meissl number)] varies from 3.4 to — 4.1; in pure cocoanut fat it varies from 47 to 50.7.*

Another method of showing the presence of cocoanut oil is to determine the volume of tenth-normal alkali required to neutralize the insoluble volatile acids from 5 grams of fat. Under the conditions described by Polenske† the results thus obtained are approx-

* Juckenack and Posternack: *Ztschr. Unters. Nahr.-Genussm.*, 1904, 7, 193.

† Polenske: *Ibid.*, 1904, 7, 273. See also — Lewkowitsch's Oils, Fats, and Waxes (3d Ed.), 853. Muntz and Coudon: *Ann. d. Inst. Agron.*, 1904; *Analyst*, 1905, 30, 155. Hesse: *Milchwirthschaftl. Centrbl.*, 1905, 1, 13; *Chem. Centrbl.*, 1905, I., 566.

imately quantitative, the percentage of insoluble volatile acids (mainly lauric acid) being much higher in cocoanut fat than in butter.

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CHAPTER XII.

Soaps and Lubricants.

Soaps, glycerol, and lubricants are the most important technical products of the fats and oils. Glycerol having been considered under the head of alcohols, methods for the examination of soaps and lubricants will be given in this chapter. Any compound of a mineral base with a fatty or resin acid may be called a soap. Since only the soaps of the alkalies are readily soluble in water, they alone are employed as detergents but insoluble soaps are frequently used as constituents of lubricating mixtures.

ANALYSIS OF COMMERCIAL SOAP.

The determinations required in the examination of a commercial soap depend largely upon the purpose for which it is intended. The scheme outlined below is adaptable to almost all cases as it can be easily extended to include additional determinations or shortened by omitting such steps as are unnecessary when only a partial analysis is required.

A cake of soap exposed to the air dries rapidly at the surface, forming a horny layer which to some extent prevents the evaporation of water from the interior. In sampling such a soap it is important to remember this variation in water content of different parts of the same cake. If the sample is to represent the individual cake as it existed at the time of commencing the analysis, a number of sections through the entire cake should be taken either by slicing or by means of a cork borer or a cheese or butter sampler. Often the purpose of the analysis is to show the composition of the sample as originally sold, in which case the dried surface should be rejected and the sample taken from the center of the cake. The sample for analysis should be reduced quickly to fine shavings and kept in a tightly stoppered bottle.

Details of Determinations Indicated in the Scheme.

I. Determination of Water.

If the soap is very hard and dry it may be reduced to fine shavings and dried on a watch-glass, heating first for some time at

OUTLINE SCHEME OF ANALYSIS.*

FIRST PORTION. Dry 2 to 5 grams of soap (I.)† and introduce into Soxhlet extractor, either in a thimble or supported by a firm plug of cotton and extract with petroleum ether.

Solution. Evaporate ether and weigh as *unsaponified fat* and *unsaponifiable matter.* (II.)	*Residue.* Allow petroleum ether to evaporate and exhaust thoroughly with boiling water.	
	Solution. Decompose with a considerable excess of standard sulphuric (or hydrochloric) acid, separate aqueous solution from fatty layer. (III.)	*Residue.* Dry and weigh as *insoluble matter.* Ignite and weigh as *insoluble mineral matter.* (X.)
	Solution. Add methyl orange and titrate for *total alkali.* Test for chlorides (or sulphates), sugar, and glycerine. (IV.)	*Fatty Layer.* Dry and weigh as *fatty and resin acids.* (V.)

SECOND PORTION. Exhaust 2 to 5 grams of the fresh sample with carefully neutralized alcohol. (VI.)

Solution. Add phenolphthalein and titrate for *free caustic alkali* or *free fatty acid.* (VII.)	*Residue.* Dry and weigh. (VIII.)		Exhaust thoroughly with boiling water.
	Solution. Divide into aliquot parts.		*Residue.* May be examined instead of residue from first portion or used for additional tests or determinations. (X.)
	Add methyl orange and titrate for *alkali carbonate* (and borate, silicate, or aluminate if present). (IX.)	Test for (and if necessary determine) *sulphate, borate, silicate,* and *aluminate.* (IX.)	

40° to 60° and then finishing at 105° to 110°. Very few soaps can be completely freed from moisture in this way but some others may be sufficiently dried for the ether extraction while the moisture determination is made on a separate sample as follows: Dissolve about two grams of soap in the minimum quantity of hot strong alcohol and evaporate on clean dry sand. Finish the drying at 110° with frequent stirring, a small rod having been weighed with the dish. For approximate determination of moisture Allen recommends Smith's method: Heat 5 to 10 grams of finely divided soap in a large porcelain crucible on a sand bath over a small Bunsen flame. Stir continually with a small glass rod (weighed

* Allen : Commercial Organic Analysis, Vol. II., Part I.

† Numbers in parenthesis refer to sections which follow.

with the crucible) having a roughened end to facilitate breaking any lumps of soap which may be formed. Continue heating until there is no more evidence of water being expelled, then test by removing the burner and placing a cold glass at once over the crucible. If no moisture condenses on the glass the soap is considered dry. With practice the drying can be finished in 20 to 30 minutes. Any burning of the soap is readily detected by the odor. The results are said to be reliable to 0.25 per cent.

II. Petroleum Ether Extract.

Transfer the thoroughly dried soap to a paper "fat extraction thimble," plug tightly with fat-free cotton and treat in a Soxhlet extractor, heated on a safety water bath or electric heater, with petroleum ether of nearly constant boiling point. Regulate the heating so that the extract fills to the syphoning point in ten or fifteen minutes and continue the extraction for four to six hours. Disconnect the extraction apparatus (observing that no free flame is near) as the solvent flows through the syphon to the flask; remove the thimble, reconnect the apparatus, and recover the solvent by placing a wide short test-tube in the space previously occupied by the thimble, or by allowing the solvent to collect in this space and removing it before it reaches the top of the syphon. Having expelled nearly all of the petroleum ether, heat the flask containing the extract in a boiling water oven to constant weight.

The petroleum ether extract of a commercially pure soap may contain unsaponified fat (or free fatty acids, which are now largely used in soapmaking) as well as the "unsaponifiable matter" of the original soap grease. Hydrocarbons, phenols, and other substances soluble in petroleum ether may also be found in mixed and "medicated" soaps. Allen* gives directions for the systematic examination of this extract including the quantitative determination of phenol if present.

III. Liberation of Fatty and Resin Acids.

Decompose the water solution of the soap by adding a considerable excess (allow 5 to 7 c.c. of normal acid for each gram of dry soap) of normal or half-normal sulphuric, nitric, or hydrochloric acid. Add the entire amount of acid at once, boil, stir thoroughly for some minutes, and keep the solution hot until the fatty

* Commercial Organic Analysis, Vol. II., Pt. I. (3d Ed.), pp. 279–284.

acids collect at the surface, leaving the water solution nearly clear, then complete the separation as in the determination of insoluble acids in butter.

It is convenient to liberate the fatty acids in a tared beaker in which they can afterward be dried and weighed (V.). If the fatty acids are liquid at ordinary temperature or form a cake too soft to be handled conveniently, a known weight of dry bleached beeswax or stearic acid may be added to the hot solution. The fatty acids become incorporated with the wax and on cooling a firm cake is obtained.

IV. Solution Separated from Fatty Acids.

This solution contains, in the form of sulphate (or chloride if hydrochloric acid be used to decompose the soap), all the alkali originally present as soap, as carbonate (silicate or borate), or as hydroxide. On titrating this solution with alkali, using methyl orange as indicator, the amount of acid found to have been neutralized gives a measure of the total alkali of the soap. Unless potash is known to be present, this total alkali is usually calculated as sodium oxide. The solution also contains any chlorides or other soluble salts, soluble fatty acids, glycerol, sugar, etc., which the soap may have contained. After titration the solution can be diluted to a known volume and separate portions taken for qualitative tests and quantitative determinations.

When sulphuric acid has been used to liberate the fatty acids, *chlorides* can be determined in a portion of the neutralized solution. If it is desired to determine both chloride and sulphate in this solution the soap can be decomposed by means of standard nitric acid. It is usually more convenient to test for sulphates in the residue from the alcohol extraction as described below.

Soluble fatty acids will be found in this solution if the liberated acids of cocoanut or palmnut oil soaps are washed with hot water, as is often recommended. When the fatty acids are separated cold and washed with cold water only, the amount dissolved can usually be neglected without appreciable error.

Sugar, if present, is detected in a part of this solution. After further treatment with acid to ensure complete hydrolysis, the invert-sugar is determined either volumetrically or gravimetrically (Chapter V.). Sugar may also be determined by means of the polariscope using a separate portion of the sample and precipitating the fatty acids as insoluble barium soaps.*

* Freyer: *Oesterr. Chem. Ztg.*, 1900, 3, 25; *Analyst*, 1900, 25, 127.

In the absence of sugar and other interfering substances, *glycerol* can be determined by treating a portion of the neutralized solution directly with sulphuric acid and standard dichromate as described in Chapter III. (Hehner's method). Since the results thus found are often too high, because of the presence of organic impurities, Lewkowitsch recommends * the following method: Decompose the water solution of the soap with sulphuric acid, separate the fatty acids, neutralize the filtrate with barium carbonate, evaporate to a syrup, and extract with a mixture of 3 parts 95 per cent. alcohol and 1 part ether. The glycerol thus obtained can be determined by the acetin method after complete removal of alcohol, but results sufficiently accurate for ordinary work can be obtained by drying, weighing, and burning the glycerol as in the analysis of fermented liquors. The method for glycerol in wines (Chapter III.) can also be used to separate glycerol from sugar in analyzing a soap containing both of these.

V. Mixed Fatty and Resin Acids.

The mixture of acids liberated as already described (III.) is dried to constant weight in a boiling water oven in a weighed flat bottomed dish or beaker as in the determination of the insoluble acids in butter fat. The weight having been found, test a portion for resin acid by the Liebermann-Storch reaction as described under drying oils (Chapter X.). In the absence of resin acids it may be possible to show the nature of the fat from which the soap was made, by examining the mixed fatty acids according to the methods used in identifying fats and oils as described in Chapters IX. and X., consulting special works such as those of Lewkowitsch or Benedikt-Ulzer for the "constants" which cannot be inferred from the properties of the corresponding fats. *The separation of fatty and resin acids* is best accomplished by *Twitchell's method* based upon the difference of behavior of these acids when exposed in alcoholic solution to the action of hydrochloric acid. By this treatment fatty acids are converted to ethyl esters while resin acids remain practically unchanged. The method is carried out by Lewkowitsch † as follows: Weigh 2 to 3 grams of the mixed acids in a flask, dissolve in 10 times their volume of absolute alcohol, immerse the flask in cold water, and pass a current of dry

* Oils, Fats, and Waxes (3d Ed.), p. 1081.

† Oils, Fats, and Waxes (3d Ed.), 394.

hydrochloric acid gas through the solution for an hour; then dilute the contents of the flask (which will have separated into two layers) with 5 times its volume of water and boil until the aqueous solution has become clear. Transfer the contents of the flask to a separating funnel by means of 50 cc. of petroleum ether (boiling below 80°); shake, allow to separate, draw off the acid solution, and wash the petroleum ether layer once with water. After the latter has separated completely and been removed, add a solution of 0.5 gram of potassium hydroxide and 5 c.c. of alcohol in 50 c.c. of water; shake, and allow to separate. The ethyl esters remain dissolved in the petroleum ether while the resin acids are extracted by the dilute alkaline solution forming soaps. Draw off the soap solution, wash the petroleum ether solution again with dilute alkali, unite the alkaline solution; liberate the resin acids by means of hydrochloric acid, collect, dry, and weigh them as in the determination of liberated fatty acids.

The resin acids can be titrated after washing free from hydrochloric acid, instead of being separated and weighed. The volumetric method is more rapid than the gravimetric but necessitates the assumption of a combining weight (346) for the resin acids, which is liable to considerable inaccuracy. According to Lewkowitsch, the results by the volumetric method are likely to be too high; those by the gravimetric method too low.

VI. Extraction with Alcohol.

Dry soap can be extracted with 95 per cent. alcohol; for wet soap stronger alcohol should be used so that after taking up the moisture of the sample it will still be too strong to dissolve an appreciable amount of carbonate. The alcohol to be used must first be very carefully neutralized, using phenolphthalein as indicator. In this neutralization there is danger of adding an excess of alkali unless it is remembered that the full pink color of the indicator will not appear in alcohol of this strength. If difficulty is experienced in detecting the neutral point a small amount of the alcohol can be removed and mixed with an equal volume of boiling water to bring out the color of the indicator.

While the extraction of the soap with alcohol is often carried out in open vessels, filtering and washing in the ordinary way, it is usually more satisfactory to use the Soxhlet extractor. The soap can be put in a paper thimble as in the petroleum ether extraction

or between plugs of cotton in a glass tube with perforated bottom. In the latter case the progress of the extraction can be watched without disconnecting the apparatus. When the extraction is complete the residue should be in powder form. If distinct pieces remain these may contain soap which has been protected from the action of the alcohol by the formation of a layer of insoluble salts. In this case remove and crush the residue, replace, and extract again.

VII. Free Caustic Alkali or Fatty Acid.

To the alcoholic extract add a few drops of neutralized phenolphthalein solution. If the solution reacts alkaline, titrate with tenth-normal acid for caustic alkali; if acid, titrate with tenth-normal alkali for free acid. For a further discussion of this extract including a rapid method for the partial analysis of soaps, see Allen, *l. c.*, pp. 291–294.

VIII. Residue Insoluble in Alcohol.

It is advisable to dry and weigh this residue so that the percentage of impurities not actually determined can be found by difference. A microscopic examination may also be of use in determining the subsequent treatment. Starch and gelatine if present could be separated from carbonate, borate, and sulphate by dissolving the latter salts in cold water; but silicate would probably be incompletely dissolved, and it is therefore better as a rule to extract with hot water and to use separate portions of the soap if necessary for the determination of starch and gelatin. In such a case extract the soap with alcohol and in the residue determine starch as described in Chapter VII., or determine nitrogen by the Kjeldahl method and calculate the corresponding amount of gelatin, taking the nitrogen content of the latter as 17.9 per cent.*

IX. Carbonate, Silicate, Borate, and Aluminate.

Add to the water extract from the residue insoluble in alcohol an excess of standard acid and boil to ensure decomposition of the silicate. If it is important to distinguish quantitatively between carbonate and the other alkaline salts present, the carbonic acid given off during this boiling can be collected and weighed. Add methyl orange as indicator and titrate with standard alkali to determine the total amount of alkali which was present as carbonate, silicate, borate, and aluminate.

* Richards and Gies: *Amer. Journ. Physiol.*, 1902, 7, 129.

To a portion of the solution add hydrochloric acid in excess, evaporate to small volume and test for boric acid by means of turmeric paper; when dry heat at 110°, take up with dilute hydrochloric acid, filter out and determine silica, if present.

Other portions of the solution or the filtrate from silica can be used for the detection and determination of sulphates, aluminates, etc.

X. Insoluble Matter.

This residue should be dried to constant weight at 100°, a portion examined microscopically and the remainder ignited and weighed. If over one per cent. of insoluble mineral matter is found it should be analyzed. Among the substances which may be found in this residue are oatmeal, bran, sawdust, clay, chalk, steatite, infusorial earth, pumice, sand, mineral pigments, etc.

Calculation and Interpretation of Results.

In the case of hard soap, the results of the partial analysis usually required may be reported as follows:

Water; unsaponified fat and unsaponifiable matter; fatty and resin anhydrides (97 per cent. of the weight of free acids); sodium oxide combined as soap; sodium hydroxide; sodium carbonate; insoluble organic matter; insoluble mineral matter. It is well to report also the total alkali in terms of sodium oxide.

The purpose for which a soap is intended must be known before an opinion as to its quality can safely be formed. In most cases the percentage of alkali combined as soap is the best measure of the amount of actual soap in the material, but for special purposes the presence or absence of other constituents is often of greater importance.

Toilet soaps should contain as little free alkali (either caustic or carbonate) as possible. Alder-Wright divided toilet soaps into three classes according to the proportion of free alkali to alkali combined as soap. The first class included those soaps which contained less than 2.5 per cent. as much free as combined alkali; the second, those in which the percentage was 2.5 to 7.5; the third, those containing over 7.5 per cent. as much free as combined alkali. In judging the quality of toilet soaps it is also important to consider the proportions and nature of all foreign matter, the amount of water, the hardness of the soap and in some cases the origin must be sought by an examination of the fatty

acids. The more expensive "transparent' toilet soaps may contain alcohol or glycerine; in cheaper grades a similar appearance is obtained by the addition of sugar.

Household soaps are made from cheaper and softer fats than those used for toilet soap. Alkali in the form of carbonate, silicate, or borate is not objectionable unless present in excessive amount. No appreciable amount of sugar or glycerine is likely to be present. Scouring soaps often contain large amounts of pulverized quartz, infusorial earth, etc., and are sometimes strongly alkaline with sodium carbonate or hydroxide.

The qualities of soaps for special and technical purposes are discussed in several of the following works.

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EXAMINATION OF LUBRICATING GREASES.

Lubricating greases are usually mixtures of soaps with fats, hydrocarbons, rosin, or tar containing water and sometimes large amounts of mineral matter. On melting, the grease often separates into a soap solution and an oily layer. The soaps used in making such lubricants may contain salts of sodium, calcium, or heavy metals with either fatty or resin acids. Some greases consisting essentially of fats and hydrocarbons melt at the temperatures to which they are subjected in use and may therefore be examined in the melted state by the methods used for lubricating oils. For most greases, however, it is necessary to adapt the analytical method to the nature of the mixture to be examined in each case, since the composition of these greases is too variable to allow the use of any fixed system of examination. It may often be necessary to resort to a combination of the methods used in the analysis of soaps, fats, and lubricating oils. For detailed information on the composition and testing of lubricating greases the reader is referred to the reference books cited at the end of this chapter and to a review by Conradson: *Journ. Amer. Chem. Soc.*, 1904, 26, 705–712.

EXAMINATION OF LUBRICATING OILS.

A thorough examination of lubricating oil involves: (1) the determination of the nature of the oil and, if it is a mixture, the proportion of each constituent; (2) tests to determine the efficiency and safety of the oil as a lubricant with special reference to the conditions of temperature, pressure, etc., to which it will be subjected in use. Among the most important properties of lubricating oils which can be measured in the laboratory are viscosity, acidity, the temperature at which the oil solidifies, and the flashing and burning points. The usefulness of other determinations will depend upon the purposes for which the oil is intended.

DETERMINATION OF CONSTITUENTS.

Pure fatty and mineral oils are largely used as lubricants, both singly and mixed with each other in all proportions. Other substances are, however, often added to reduce the cost or to increase viscosity of the oil, among the most common being rosin oils and "gelatin oils" containing aluminum oleate or other soaps. A better but more expensive means of increasing viscosity is to use castor oil or a "blown" oil.

In beginning the examination of a lubricating oil, note carefully any color, odor, turbidity, or fluorescence which may aid in identifying the oil or detecting foreign substances. The presence of soap is easily shown by igniting a portion of the oil, as refined fatty and mineral oils should not yield over 0.05 per cent. of ash. Rosin oil can be detected by the Liebermann-Storch reaction.

After making these preliminary observations the saponification number should be determined as this may show the sample to be a practically pure fatty or mineral oil. In saponifying mixtures consisting largely of heavy mineral oil there is difficulty in securing sufficient contact between the sample and the alcoholic potash solution even though petroleum ether or gasoline be added. In such cases a Soxhlet extractor can be placed between the flask and the reflux condenser.* The intermittent syphoning of the condensed solvent from the extractor into the saponification flask mixes the contents and facilitates saponification. In order to diminish the volume of solvent required and the interval between stirrings, the body of the extractor is filled with glass beads. Having found the saponification number (Chapter IX.), if the sample appears to be a mixture of fatty and mineral or rosin oil the proportions of saponifiable and unsaponifiable matter are found either by separating and weighing the latter or by estimating the former from the amount of fatty acids recovered from the soap solution after saponification.

Determination of Unsaponifiable Oils.

Weigh 2 to 10 grams of oil (depending upon the saponification number and the method to be followed), saponify by heating with alcoholic potash on a water bath,† evaporate off the alcohol,

* Conradson: *Journ. Amer. Chem. Soc.*, 1904, 26, 672.

† See also the method involving cold saponification given by Fahrion: *Ztschr. angew. Chem.*, 1898, 267.

and separate the unsaponifiable matter by one of the following methods.

Method of Immiscible Solvents. — To the residue from the evaporation of alcohol add 75 c.c. of water, stir thoroughly, transfer to a separatory funnel, add about an equal volume of petroleum ether or washed ethyl ether, close the funnel, shake vigorously, and allow to stand over night or until the aqueous and ethereal solutions separate completely. Draw off the aqueous layer into another separatory funnel; wash it again with ether and the ethereal layer again with water; repeat if necessary. Finally unite the ether solutions in a weighed flask, distil off the ether, and dry the unsaponifiable oil to constant weight in a boiling water oven.

If desired, the fatty acids can be recovered from the aqueous soap solution by adding an excess of mineral acid and shaking with ether or by separating the fatty acids as in soap analysis.

The principal objection to the separation by immiscible solvents is that emulsions frequently form in the separating funnel which remain even on standing for a day or more. The addition of 1 to 2 c.c. of alcohol often helps to break the emulsion but if more alcohol is added it tends to carry soap into the ether layer. The separation of the solvents is also facilitated by chilling the funnel and twirling it gently or, if the apparatus is available, by whirling in a centrifuge. Petroleum ether dissolves less soap than ethyl ether and gives less troublesome emulsions but does not always extract the unsaponifiable matter completely.

Extraction of the Dry Soap. — To avoid difficulties of the preceding method, A. C. Wright * recommends the following: Saponify 10 grams of oil using 5 grams of caustic potash; after evaporating off the alcohol, add 8 grams of sodium bicarbonate and 20 c.c. of pure methyl alcohol, stir well and evaporate, add 10 c.c. more of methyl alcohol and 25 grams of precipitated chalk, mix well, dry on a water bath and then for a few minutes at 110°. Transfer the thoroughly dried mixture quickly to a Soxhlet extractor and extract the unsaponifiable matter with petroleum ether. Dry the extract to constant weight in a boiling water oven and weigh.

The mixture of calcium carbonate and soap from which the unsaponifiable matter has been extracted can be treated with hydrochloric acid to dissolve the carbonate and liberate the fatty acids which can then be separated and examined further.

* Analysis of Oils and Allied Substances, p. 111.

Estimation and Identification of Fatty Oils.

From the weight of fatty acid recovered as described above, the percentage of fatty oil can be calculated on the assumption that the oil yields 95 per cent. of insoluble fatty acids. The result thus found serves as a check upon the direct determination of unsaponifiable oil.

If only fatty and mineral oils are present and the percentage of the former is small, it can be estimated with sufficient accuracy for most purposes from the saponification number, since the fatty oils which are likely to be present in mixed lubricants do not vary greatly in their saponification numbers. See table at end of Chapter IX. If the fatty oil is identified the average number for that species of oil should be used in estimating the percentage.

If the lubricant consists entirely of fatty oil with a known small amount of inert unsaponifiable matter, the usual methods for the identification of fatty oils can be employed. Otherwise the identification is based upon the examination of the separated fatty acids.

Viscosity.

Apparatus and Methods.

The viscosity of an oil can be determined either by measuring the resistance which it offers to the movement of a submerged solid, or by observing the rate at which it flows through an aperture under given conditions of temperature and pressure. Torsion viscosimeters such as that of Doolittle * depend upon the first principle but those depending upon the measurement of the rate of flow are much more generally used. Viscosimeters of this kind are made in a great variety of forms for descriptions of which the reference books at the end of the chapter can be consulted. Among the viscosimeters most commonly used in the United States are those of Redwood, Engler, and Saybolt.

Redwood's viscosimeter consists of a cylinder about 4.7 cm. in diameter and 8.7 cm. high, having in the center of the bottom a cup-shaped agate jet which can be closed by means of a spherical plug. Inside the cylinder is a small fixed bracket of thick bent wire with an upturned point to indicate the height to which the oil should extend at the beginning of the test. The apparatus is jacketed and provided with a closed side tube and a revolving

* *Journ. Amer. Chem. Soc.*, 1893, 15, 174.

stirrer so that determinations can be made at high temperatures if desired. The apparatus is intended to deliver 50 c.c. of water at 15.5° in 25.5 seconds, but as the rate of flow is influenced by many conditions it must be determined by each observer for his own apparatus and method of working. The instrument must be very carefully cleaned and dried before and after using as any dust (or scratches caused by careless cleaning) in the agate jet will alter the rate of flow.

To use the apparatus at room temperature place it on a level support, insert the plug, and fill with the liquid to be tested until the surface comes exactly to the upturned point already mentioned. Place beneath the outlet a narrow-necked flask graduated at 50 c.c., open the jet by lifting the ball valve, and observe the time required for 50 c.c. to flow into the receiving flask. A stop watch is recommended but is not absolutely essential. Repeat the determination as often as is necessary to obtain an average result having a probable error of less than 2 per cent. Whatever method is adopted for expressing the results,* the report should always show the actual time of flow for the oil and for water and the temperature at which the test was made.

In working at any temperature other than that of the room, fill the outer jacket of the viscosimeter with water, or for temperatures above 95° with mineral oil. This is first brought to the required temperature, the oil to be tested (previously brought to the same temperature) is then introduced and the receiving flask is placed in a bath of liquid at the temperature at which the test is to be made. At high temperatures great care must be taken in heating and stirring as a variation of 1° or less will sometimes make an appreciable difference in the time of flow.

The Redwood viscosimeter is generally regarded as standard in Great Britain having been adopted† by the War Department, the Scottish Mineral Oil Association, and the principal railway companies. Engler's viscosimeter occupies a similar position in Germany and the "normal apparatus" of this form is now manufactured under the joint control of the Charlottenburg Mechanisch-technische Versuchsanstalt and the Karlsruhe Chemisch-technische Versuchsanstalt. For description and illustration of this apparatus

* Results are sometimes compared with standard rape oil requiring 535 seconds at 15.5°. Other methods of expressing viscosity are given by different writers; see references at the end of the chapter.

† Lewkowitsch: Oils, Fats, and Waxes (3d Ed.), p. 199.

see Lewkowitsch's Oils, Fats, and Waxes (3d Ed.), pp. 202–204. Directions for use are furnished with each apparatus. For a description of Saybolt's viscosimeter which is made in three forms for testing different types of oils consult Gill's Oil Analysis (3d Ed.), pp. 24–28.

Significance of Results.

Since the object of lubricating with oil is to separate the moving surfaces by a fluid layer, it is important that the oil have sufficient viscosity or "body" to stay in place and keep the moving surfaces apart under the maximum pressure to which they will be subjected. The greater the pressure the more viscous the oil should be, but any viscosity beyond that which is necessary to keep the oil in place means an increase of fluid friction and consequent loss of power. The viscosity of the oil is therefore the most direct indication of its suitability as a lubricant under given conditions. For several reasons, however, the viscosity alone is not a conclusive measure of the lubricating power. The adhesion to solid surfaces which prevents the displacement of the oil by pressure is not always directly proportional to the true viscosity or internal friction. Oils vary greatly in the rate of change of viscosity with increasing temperature and pressure. The viscosity as measured by the rate of flow depends not only upon the internal friction of the oil, but also to some extent upon its adhesion to the sides of the outlet and upon the specific gravity. Hence it is not to be assumed that any two oils having the same viscosity can be used interchangeably as lubricants. In order to duplicate an oil which has been found satisfactory in use, the kind of oil, the specific gravity, and the viscosity shall all be specified.

Viscosity is especially important in dealing with mineral oils because of the ease with which they can be varied in this respect, while any particular kind of fatty oil varies only within comparatively narrow limits. For a full theoretical discussion of viscosity and lubrication the work of Archbutt and Deeley should be consulted. The reader must also be referred to this and other books and articles given below for discussion of the many practical considerations affecting the selection of lubricating oils.

ACIDITY.

Weigh accurately 5 to 10 grams of oil in a 250 c.c. Erlenmeyer flask, add 50 c.c. of neutralized 85 per cent. alcohol containing

phenolphthalein as indicator and titrate with standard sodium or potassium hydroxide shaking vigorously after each addition until a permanent pink color is obtained. It is often necessary to allow the flask to stand after shaking until the oil separates from the alcohol solution before observing the color of the latter.*

To test for free mineral acid, shake 10–15 grams of oil with 100 c.c. of warm water in a separatory funnel, allow to separate, draw off the water, filter through wet paper, cool, and add methyl orange. If mineral acid is found, shake the oil remaining in the funnel repeatedly with small portions of hot water until all mineral acid is extracted, filter as before, add the filtrate to the first portion containing methyl orange and titrate very carefully with standard alkali. Concentrate the neutralized solution, test qualitatively to determine the nature of the acid and calculate the percentage. If the identification of the mineral acid is prevented by the presence of salts, calculate the mineral acidity as due to sulphuric acid. The acidity due to organic acids, or the total acidity if only this is determined, is usually calculated as percentage of oleic acid. As much as 15 per cent. of free oleic acid is sometimes allowed in lubricating oils. The best grades of lard oil do not contain over 1.5 per cent. Free mineral acids should be absent.

Cold Test and Chilling Point.

The "cold test" indicates the temperature at which the sample is just sufficiently melted to flow; the "chilling point" that at which the oil begins to become turbid or to show flocks or scales of solid. In either case the temperature required will be influenced by details of manipulation, so that an arbitrary method must be followed to obtain strictly comparable results. The following directions follow the procedure of the Pennsylvania railroad laboratory.†

Cold Test. — Pour about 25 c.c. of oil into an ordinary sample bottle of about 100 c.c. capacity and introduce a short stout thermometer. Place the bottle in a freezing mixture until the sample

* For determining acidity in very dark colored fats the use as indicator of 10 c.c. of a 2 per cent. solution of "Alkali Blue II OLA" (Meister, Lucius and Brunig) in 99 per cent. alcohol has been recommended by Freundlich: *Oesterr. Chem. Ztg.*, 1901, 4, 441; *Ztschr. Unter. Nahr.-Genussm.*, 1902, 5, 460.

† Motive Power Department Specifications, No. 75, Altoona, Pa., 1895. For the method and apparatus of the Chicago, Burlington and Quincy railroad laboratory see Stillman's Engineering Chemistry, 2d Ed., pp. 352–354.

is solid throughout. Remove the bottle and allow the solidified oil to soften, stirring and mixing by means of the thermometer until the mass will flow from one end of the bottle to the other. The reading of the thermometer at this point is the "cold test."

Chilling Point. — Usually it is only necessary to know whether the oil remains clear for a given number of minutes at a given temperature. Use the same bottle, amount of sample, and thermometer as for the cold test. Expose the liquid to cold, stirring with the thermometer and hold at the required temperature for the specified time (usually ten minutes). If the oil remains transparent and free from flocks or scales, it meets the requirement as to chilling test.

If it is required to find the chilling point the procedure is similar, but the liquid after remaining clear as described is exposed to a temperature 3° lower, allowed to stand with constant watching and occasional stirring with the thermometer until the oil is as cold as the bath, repeat this cooling until opacity or flocks or scales begin to show. The reading of the thermometer when this occurs shows the "chilling point."

For further information on the cold test or setting point see the works of Archbutt and Deeley, Gill, Holde, Lewkowitsch, and Stillman.

Flashing and Burning Points.

For the most accurate results closed testers such as are used in examining illuminating oils should be employed, but as such accuracy is not required in testing lubricants it will usually be sufficient to carry out the test without the use of any special apparatus as follows:*

On a sand bath and partly imbedded in it place a porcelain dish about 6.5 cm. in diameter and 2.5 cm. deep. Fill the dish to about 0.6 cm. of the top with the oil to be tested and hang a thermometer so that the bulb is immersed in the oil at the center of the dish without touching the bottom. Heat by means of a Bunsen burner and as the flashing point is approached test at each third or fourth degree by passing the test flame slowly entirely across the dish about 1 cm. above the level of the oil and directly in front of the thermometer. Record the temperature at which the first flash is seen as the *flashing point.* Continue heat-

* Specifications of the Pennsylvania Railroad Motive Power Department, Altoona, Pa., 1902.

ing and testing in the same way until the liquid takes fire; note the temperature as the *burning point.* Remove the thermometer and blow out the flame or smother it by sliding a watch glass over the dish.

The test must be made in a place protected from drafts. The test flame should be about 0.5 cm. long and is conveniently obtained from a narrow glass jet connected with the ordinary gas tubing. The flow of gas is easily regulated to give a flame of the required size. The heating of the sandbath should be so regulated that the temperature of the oil rises 6° to 8° per minute, the rise being more rapid the higher the flashing point. The test flame can then be applied every half minute.

Any variation from the conditions given, either in the size and form of dish, the rate of heating and testing, or the manner of applying the test flame may cause an appreciable discrepancy in the result.

Additional Determinations.

Additional tests and determinations are frequently required to show the suitability of the lubricant for the particular use intended. *Friction tests* on oil testing machines especially designed for the work are sometimes of great importance. A full discussion of such mechanical methods of testing will be found in Archbutt and Deeley's Lubrication and Lubricants.

Loss by evaporation and tendency to "gum" are tested by heating a small amount of oil on a watch glass for several hours at the highest temperature to which it is likely to be subjected in use. The oil must not become sticky and the loss of weight should usually be less than one per cent. *Suspended matter* which may be invisible in a dark oil is detected by diluting the sample with gasoline or petroleum ether. *Antiflourescents* added to destroy the fluorescence or "bloom" of mineral oils can often be detected by boiling 1 c.c. of the oil with 3 c.c. of a 10 per cent. solution of potassium hydroxide in alcohol. A red color indicates nitronaphthalene or nitro-benzene, which are the principal antifluorescents used. According to Holde * asphalt pitch is used to thicken cylinder oil and can be approximately determined as follows: Dissolve 5 grams in 125 c.c. of ether at 15°, add, drop by drop with constant shaking, 62.5 c.c. of 96 per cent. alcohol; after standing 5

**Mitt. Kgl. Techn. Versuchsanstalt, Berlin,* 1902, 20, 253; *Ztschr. Unters. Nahr.-Genussm.*, 1903, 6, 855.

hours at 15°, filter, wash with a mixture of alcohol and ether (1 : 2 by volume) until nothing more than traces of pitch-like substance is removed. Dissolve the residue in benzol, evaporate, dry one half hour at 105°, and weigh.

For other tests and determinations and fuller discussions of most of those here given the reader is referred to the works given for reference below.

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CHAPTER XIII.

Proteids and Cereals.

PROTEIDS AND RELATED COMPOUNDS.

The proteids are very complex and usually amorphous compounds, differing in composition and properties, but all of high molecular weight and unknown chemical structure. They all contain carbon, hydrogen, nitrogen, sulphur, and oxygen; some also contain phosphorous and a comparatively small number iron. The limits of ultimate composition of the well-known simple proteids are as follows: *

Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.
51.3–55.0	6.7–7.3	15.5–19.3	0.3–2.2	20.8–23.5 per cent.

Proteids differ in their solubilities in water, salt solutions, and alcohol but are all insoluble in ether, chloroform, carbon tetrachloride, carbon bisulphide, benzene, and petroleum ether.

The proteid compounds are of the greatest importance in physiology and food chemistry, being the fundamental organic constituents of the living substance of both animal and vegetable cells, and the only group of organic compounds which is strictly essential to the nutrition of all animals. The proteids and closely related compounds have therefore been studied and classified largely from the physiological standpoint. While differences exist both in classification and terminology, the following is believed to represent the present usage of the majority of English-speaking physiologists and physiological chemists.†

Simple Proteids.

Albumins. — Soluble in water and dilute salt solutions; precipitated by adding sufficient alcohol or by saturating the aqueous solution with ammonium sulphate. The water solutions are

* Ultimate analyses of a number of proteids have recently been compiled and discussed by Osborne: *Journ. Amer. Chem. Soc.*, 1902, 24, 160.

† Compare American Text-book of Physiology and reference books given at the end of the chapter.

coagulated by heating, usually at 70°–73° (Halliburton), but sometimes much lower, leucosin coagulating at 52° (Osborne).

Globulins. — Insoluble in pure water but soluble in dilute salt solutions. Precipitated by alcohol or by saturation with ammonium or magnesium sulphate; also precipitated from salt solutions on removing the salt by dialysis. Some of the vegetable globulins are distinctly crystalline and not coagulable by heating.

*Alcohol Soluble Proteids.** — These occur especially in the cereal grains. Gliadin, insoluble in water, dilute salt solution, or absolute alcohol, but soluble in 75 per cent. alcohol is the best-known member of this group.

Albuminates. — By the action of acid or alkali upon native or coagulated proteid the latter is converted into an acid- or an alkali-albumin or albuminate. Both acid and alkali albuminates are nearly insoluble in water and dilute salt solution, but usually dissolve readily in water containing a very small amount of acid or alkali and are precipitated from such solutions by neutralization at ordinary temperature. The albuminates are precipitated from nearly neutral solutions by the general precipitants for soluble proteids (see below); but a very minute amount of acid or alkali is sufficient to prevent the coagulation of albuminate by boiling. Acid albumin, also called *syntonin*, is formed by the acid of gastric juice as the first step toward peptic digestion.

Proteoses and Peptones. — These are products derived from other proteids by digestion or by simple hydrolysis. They are soluble in water and not coagulated by boiling their aqueous solutions. No sharp line can be drawn either between proteoses and peptones or between peptones and the simpler nitrogen compounds which result from prolonged digestion. As the terms are generally used, *peptones* may be considered the final products of digestion or hydrolysis which are still proteids as judged by the biuret reaction (see below) and are precipitable by tannin (perhaps not always completely) or by addition of strong alcohol. *Proteoses* (albumoses) are intermediate products between albuminates and peptones. In addition to the proteid reactions shown by peptones the proteoses are precipitated from aqueous solutions at ordinary temperatures by adding acetic acid and potassium ferrocyanide or by saturating the solution with zinc or ammonium sulphate.

* The classifications commonly given relating especially to animal proteids omit this group.

The term peptone was formerly applied to all digestion products not coagulated by boiling and is still popularly used in the same sense, the best commercial "peptones" consist largely of proteoses.

Coagulated Proteids. — This group includes proteids which have been coagulated by heating or by the action of reagents or enzymes. The nature of the changes which take place in coagulation is not known. The coagulated proteids are insoluble in water, alcohol, salt solutions, or very dilute acids. They are dissolved and converted into albuminates by acids and alkalies especially on heating.

Some plant proteids such as the glutenin of wheat are insoluble in the neutral solvents but dissolve readily in very dilute alkali. These may be native insoluble proteids or they may have been coagulated by an enzyme in the plant.

Combined Proteids.

Chromo proteids. — There are compounds of simple proteids with coloring matter usually containing iron. Hæmoglobin and its derivatives are the best-known examples.

Glyco-proteids. — Glyco- or gluco-proteids are compounds of proteids with carbohydrates. They are practically insoluble in water but easily soluble in very weak alkalies. On boiling with dilute mineral acids they yield considerable amounts of reducing sugars. Mucins and mucoids belong to this group.

Nucleo-proteids. — These are compounds of proteids and nuclein or nucleic acid, an organic acid yielding phosphoric acid on decomposition. True nuclein also yields on decomposition one of the purin bases and is thus distinguished from paranuclein which it resembles in other respects. Nucleo-proteids are found especially in cell nuclei and are therefore particularly abundant in the highly nucleated cells of secreting organs such as the liver, pancreas, etc.

While all of the simple proteids are lævorotatory, the nucleo-proteids thus far studied* have shown dextro-rotation and the nucleic acid of the wheat embryo has been found to be strongly dextrorotatory.†

Paranucleo-proteids or Nucleo-albumins. — These compounds of proteids with paranuclein are often classified as a sub-group of the true nucleo-proteids which they resemble closely in composition. Recently, however, the purin bases have been extensively studied

*Gamgee and Jones: *Amer. Journ. Physiol.*, 1903, 8, 447.

†Osborne: *Ibid.*, 1903, 9, 69.

and shown to be of much physiological importance, and since paranucleins do not yield purin bodies on decomposition, the paranucleoproteids are now frequently classified as an independent group under the name of nucleo-albumins and are sometimes considered as simple proteids containing phosphorus. Casein and vitellin (the phosphorus-containing proteid of egg yolk) are examples of this group.

Albuminoids (Albumoids, Proteoids, Gelatinoids).

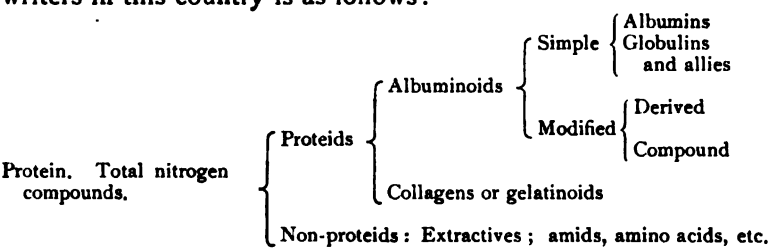
This division includes several groups of compounds differing considerably from each other but all closely related to the true proteids included in the above groups and all characterized by their resistance to reagents. They are apparently formed from proteids in the body but cannot take the place of proteids in nutrition. Among the more important of the albuminoids are *collagens* which yield *gelatins* on boiling with water; *keratins* of skin, horn, hair, feathers, nails, etc.; *elastin* of connective tissue; *skeletins*, the nitrogenous compounds of the skeletal and related tissues of invertebrates, including the characteristic compounds of sponges and silk.

Gelatins (and collagens) are the only albuminoids which are likely to be met in connection with the true proteids in foods, etc., so that the other substances mentioned need not be considered in connection with the terminology and reactions given below.

Other Nitrogen Compounds — Terminology.

Among the organic nitrogen compounds which occur with proteids in many animal or vegetable substances are the lecithins and related compounds, alkaloids, and the so-called "nitrogenous extractives" including amines, amids, and amino-acids. Ammonium salts and nitrates may occur in plant and animal tissues but usually only in minute amounts. They may, however, be added to food materials as preservatives. In most natural food products the total amount of these simpler nitrogen compounds is small as compared with that of proteids and it has become customary in food analysis to take the total nitrogen as a measure of the proteids present, so that the percentage of proteids as reported ordinarily means the percentage of nitrogen multiplied by 6.25, this factor being based on the assumption that proteids contain approximately 16 per cent. of nitrogen.

Protein is the term now commonly used to designate the results thus arbitrarily estimated from the nitrogen content, *proteids* being preferably reserved as a general name to cover the simple and combined proteids (and sometimes also gelatin) while the simpler nitrogen compounds are grouped together as *non-proteids*. Beyond this division into proteids and non-proteids the terminology of the nitrogen compounds of foods is in a very confused state. That recommended by the Association of American Agricultural Colleges and Experiment Stations and largely used by agricultural writers in this country is as follows:*



The most important point to be noted here is the use of the word "albuminoids." Formerly this was used synonymously with proteids to designate (1) simple and combined proteids and (2) gelatin and related compounds. As the differences between these two classes of compounds has become better known the majority of physiologists and physiological chemists have confined the term albuminoids to the latter class in order to distinguish these compounds from the true proteids, while in the agricultural terminology just quoted the compounds of the first class are called albuminoids. Some writers propose to discard the term "albuminoids" entirely, retaining "simple and combined proteids" and using for the related compounds some new term such as "proteoids" or "albumoids."

General Reactions of Proteids.

Color Reactions.

Among the most important color reactions are:—

1. *The xanthoproteic reaction.* — Proteids are colored yellow by nitric acid of 1.2 specific gravity or stronger. The color is intensified by heating and changes to orange or red on treatment

* U. S. Dept. Agriculture, Office of Experiment Stations, Bull. 65, p. 117; Armsby's Principles of Animal Nutrition, p. 7.

with an excess of ammonia. According to Halliburton * this reaction depends upon the presence of an oxybenzene nucleus.

2. *Millon's Reaction.* — On heating with Millon's reagent † (a solution of mercuric nitrate containing nitrous acid) proteid matter (including gelatin) gives a brick-red coloration which according to Nasse is also due to the presence of any oxybenzene nucleus in the proteid molecule. For detailed discussions of this reaction the papers of Vaubel ‡ and Nasse § should be consulted.

3. *Adamkiewicz' or Tryptophan reaction.*—When proteid is treated first with glacial acetic acid and then with concentrated sulphuric a violet color usually appears. Hopkins and Cole || found that the reaction occurred only when the acetic acid contained traces of glyoxylic acid and that a better reaction is obtained by mixing the proteid with a little glyoxylic acid solution¶ and afterward adding concentrated sulphuric acid. The color then appears at the line of contact of the liquids. Gelatin does not give the reaction (Hammarsten). According to Osborne and Harris ** the vegetable proteids vary greatly in their reactions, some of them giving little if any violet color. This reaction is due to the presence of the tryptophan group in the proteid molecule, tryptophan being probably skatol-amido-acetic acid (Hopkins and Cole).

For other color reactions due to tryptophan see Cole: *Journ. Physiol.*, 1903, 30, 311.

4. *Piotrowski or Biuret Reaction.*—On adding a very dilute solution of copper sulphate drop by drop to a proteid solution strongly alkaline with sodium or potassium hydroxide a rose-red to violet coloration appears. A more pronounced rose color is obtained with proteoses and peptones than with other proteids. To test for

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* Schäfer's Textbook of Physiology, I., 47.

† To prepare the reagent dissolve mercury in twice its weight of nitric acid, 1.42 sp. gr., and dilute the solution obtained with three times its volume of water. According to Nasse a better method is to use a solution of mercuric acetate containing a few milligrams of sodium or potassium nitrite, the solution having been recently acidulated with acetic acid.

‡ *Ztschr. angew. Chem.*, 1900, 1125.

§ *Arch. ges. Physiol.* (*Pflüger*), 1901, 83, 361.

|| *Proc. Royal Soc.*, 1901, 68, 21; *Journ. Physiol.*, 27, 418; 29, 451.

¶ Prepared as follows: Place a saturated solution of oxalic acid in a tall cylinder, add lumps of sodium amalgam (about 60 grams per liter of solution), allow to stand as long as hydrogen is evolved then filter and dilute the solution with twice its volume of water.

** *Journ. Amer. Chem. Soc.*, 1903, 25, 853.

peptones in a solution containing other proteids,* precipitate the latter by saturation with zinc sulphate, filter, to the filtrate add caustic soda until the zinc hydroxide first precipitated is completely dissolved, then add a few drops of a one per cent. solution of copper sulphate. This test is said to show as little as 1 part of peptone in 100,000 of solution. For other proteids it is less delicate. The reaction is given by many substances other than proteids; according to Schiff† by any compound containing two amino groups united either directly by their carbon atoms or by means of a third carbon or a nitrogen atom. Examples of these three classes of compounds are oxamid, malonamid, and biuret.

To establish the presence of proteid all of these tests should be applied since any one of them may be given by substances other than proteids. By combining color reactions with some of the precipitation reactions given below conclusive evidence of the presence of proteid can be obtained.

Precipitation Reactions.

Coagulation by heating and precipitation by *saturation with zinc or ammonium sulphate* have been mentioned in describing the different groups. It should be noted that the presence of other nitrogen compounds including urea, pyridine, and piperidine interferes with the coagulation of proteids.‡

Nitric or *metaphosphoric acid* precipitates most proteids other than peptones. *Potassium ferrocyanide* precipitates all true proteids other than peptones from solutions acidulated with acetic acid. Gelatin is not precipitated. *Copper, lead,* and other heavy metals form insoluble compounds with proteids. Basic lead acetate is much used to remove proteids from solutions to be examined in the polariscope and cupric hydroxide has been commonly employed for the separation of proteids from amids in vegetable foods. *Tannin* in the presence of salt precipitates proteids, including peptones, completely (Allen).§ *Phosphotungstic acid* in the cold precipitates proteids and simpler nitrogen compounds, especially the diamino-acids; in hot solutions small amounts of peptones and simpler compounds are not precipitated. *Bromine* added to saturation precipitates proteids including peptones and gelatin. According to Allen the precipitation is quantitative.

* Neumeister: *Ztschr. Biol.*, 1890, 26, 324.

† *Ber. deut. chem. Ges.*, 1896, 29, 298; Hammarsten-Mandel, p. 31.

‡ Spiro: *Ztschr. physiol. Chem.*, 1900, 30, 182.

§ The completeness of the precipitation of peptones is sometimes questioned.

As most of these precipitation reactions are also given by alkaloids, and some of them by amino-compounds, it is important in order to show the presence of proteids to precipitate with as many reagents as possible. The precipitates obtained by heat coagulation and by acetic acid and potassium ferrocyanide * should be tested for the color reactions described above. For other precipitation reactions see Halliburton: Schäfer's Textbook of Physiology, I., Chapter I., and Cohnheim: Chemie der Eiweisskörper. The completeness of precipitation by several of the reagents mentioned, and the interference of other substances are discussed in the papers cited at the end of the next section.

Separation of Proteids from Simpler Nitrogen Compounds and from Each Other.

The separation of proteids from simpler nitrogen compounds is usually based upon the precipitation of the former by some reagent which will not precipitate the other nitrogen compounds present in the substance under examination. The choice of precipitant will therefore depend upon the nature of the substance in which proteid is to be determined. Cupric hydroxide has been most commonly used for vegetable, and tannin, phosphotungstic acid, or bromine for animal substances.

The methods of separating proteids from each other are based almost entirely upon differences in solubilities and coagulation or other precipitation reactions such as have been given in characterizing the groups already mentioned. As the reactions of the peptones approach those of some of the compounds of known structure, the separation of proteids from simpler compounds and from each other can best be studied as parts of the same problem. The methods available for these separations are so dependent upon the particular combination of compounds to be separated that any attempt to give detailed directions would be of less value than references to the original publications among the more important of which are the following: —

Stutzer: Untersuchungen ueber die quantitative Bestimmung des Proteinstickstoffes und die Trennung der Proteinstoffe von anderen in Pflanzen vorkommenden Stickstoffverbindungen, *Journ. f. Landwirthschaft*, 1880, 28, 103; 1881, 29, 473; 1886, 34, 151.

Schulze und Barbieri: Zur Bestimmung des Eiweisstoffe und

* Winternitz: *Ztschr. physiol. Chem.*, 1892, 16, 439.

der nichteiweissartigen Stickstoffverbindungen in der Pflanzen, *Landw. Vers. Stat.*, **26**, 218.

Teller: The Quantitative Separation of Wheat Proteids, Bul. 42, Ark. Agl. Expt. Sta., p. 81 (1896).

Allen and Searle: Improved Method of Determining Proteid and Gelatinoid Substances, *Analyst*, 1897, **22**, 258.

Baumann und Bömer: Ueber die Fallung der Albumosen durch Zinksulfat, *Ztschr. Unters. Nahr.-Genussm.*, 1898, **1**, 106.

Mallet: Analytical Methods for Distinguishing between the Nitrogen of Proteids and that of the Simpler Amids or Amino-acids, Bul. 54, Div. Chem., U. S. Dept. Agriculture; *Chem. News*, 1899, **80**, 117, 168, 179.

Vivian: A Comparison of Reagents for Milk Proteids, 16th Ann. Rpt. Wis. Agric'l. Expt. Sta., p. 179 (1899).

Barnstein: Ueber eine Modifikation des von Ritthausen vorgeschlagenen Verfahrens der Eiweissbestimmung, *Landw. Vers. Stat.*, 1900, **54**, 327; *Ztschr. Unters. Nahr.-Genussm.*, 1901, **4**, 688.

Schjerning: [A series of papers on the quantitative separation and precipitation of proteids], *Ztschr. anal. Chem.*, 1894, **33**, 263; 1895, **34**, 135; 1896, **35**, 285; 1897, **36**, 643; 1898, **37**, 73, 413; 1900, **39**, 545, 633.

Fraps and Bizzell: Methods of Determining Proteid Nitrogen in Vegetable Matter, *Journ. Amer. Chem. Soc.*, 1900, **22**, 709.

Hart: Ueber die Quantitative Bestimmung der Spaltungsprodukte von Eiweisskörpern, *Ztschr. physiol. Chem.*, 1901, **33**, 347.

Van Slyke and Hart: Methods for the Estimation of the Proteolytic Compounds contained in Cheese and Milk, Bul. 215, New York Agl. Expt. Sta., *Amer. Chem. Journ.*, 1903, **29**, 150.

Bigelow: Meat and Meat Products, U. S. Dept. Agriculture, Bur. Chem., Bul. 65, pp. 10, 17; Bul. 13, Part 10, p. 1396; Bul. 81, p. 104.

Grindley: A Study of the Nitrogenous Constituents of Meats, U. S. Dept. Agriculture, Bur. Chem., Bul. 81, p. 110, *Journ. Amer. Chem. Soc.*, 1904, **26**, 1086.

Chamberlain: Determination of Gliadin and Gutenin in Flour, U. S. Dept. Agriculture, Bur. Chem., Bul. 81, p. 118; Circular 20, p. 14

Grindley and Emmett: The Chemistry of Flesh, *Journ. Amer. Chem. Soc.*, 1905, **27**, 658.

CEREALS AND OTHER GRAINS — MILL PRODUCTS.

In the analysis of these products as of other foods and feeding stuffs of vegetable origin the constituents usually determined are moisture, fat, proteid, fiber, and ash. The remaining constituents, estimated by difference, constitute the so-called nitrogen-free extract composed mainly of carbohydrates. When little fiber is present its determination is frequently omitted, in which case fiber and nitrogen-free extract are reported together, usually as "carbohydrates by difference." When a further examination of any one of these groups of compounds is desired it can be made according to the methods already described. The fat obtained by extraction with ether can be studied as outlined in Chapters IX. to XI., the separation of the nitrogen compounds has been discussed in the preceding part of this chapter, and methods for the determination of the principal carbohydrates are given in Chapters V. to VII. The present outline will therefore be confined to the determinations first mentioned. Samples for analysis should be air-dried and ground to pass a sieve of one half millimeter mesh, though for very resistant substances a sieve having round holes of one millimeter diameter may be used.

Determination of Moisture and Fat.

Dry 2 grams for 5 hours, or to constant weight, at the temperature of boiling water, if possible in a current of dry hydrogen or in vacuo. Consider the loss of weight as moisture. Extract the dried sample in a Soxhlet or continuous extractor, with anhydrous alcohol-free ether for sixteen hours. Dry the extract to constant weight in a boiling water oven. The ether extraction should be carried out at a distance from any free flame, the flask being heated by a safety water bath or, more conveniently, by an electric heater.

Notes. — The ether extract of vegetable substances often contains in addition to fat more or less of coloring matters and resinous substances, these being more readily soluble in ether containing fatty oils than in ether alone. In the cereal grains and especially in the milling products from which the outer layers of the grains have been separated the amount of such impurities is usually negligible. If the ether extract is made to percolate a layer of animal charcoal, practically pure fat is obtained.*

* Patterson: *Amer. Chem. Journ.*, 12, 261.

The reason for drying in a current of hydrogen rather than in air is that the oils of the cereal grains belong to the "semidrying" group and therefore absorb oxygen when exposed to air, especially at high temperature. This will of course increase the weight of the fat and make the apparent percentage of moisture too low. The partially oxidized oils are also apt to be incompletely extracted by ether. For a full discussion of the determination of water in foods and physiological preparations, see Benedict and Manning: *Amer. Journ. Physiol.*, 1905, 13, 309.

Fat may also fail of complete extraction, even when unchanged, by being occluded or mechanically enclosed in carbohydrate or proteid material which is impervious to the ether.

Although ether extracts may be evaporated at the temperature of boiling water without loss of fat, such loss has been found to occur in drying moist samples even in a current of hydrogen. That the loss in such cases is, in part at least, due to an actual volatilization of material may be shown by passing the current of hydrogen in which the sample is dried into strong sulphuric acid. This loss is probably due to the action of the escaping steam and may be practically avoided by drying at a lower temperature, preferably in a partial vacuum.

All three of the causes just mentioned tend toward a deficiency of fat in the analysis of cooked foods prepared from cereal products. Thus in a number of experiments on bread making * the fat found by analysis of the dried bread was less than half of that contained in the materials used and the iodine figure of the ether extract of the bread was only 60.4 as against 101.4 in that of the original flour showing that a very considerable oxidation had taken place even in that portion of the fat which was still soluble in ether.

Berntrop's method for the determination of fat in breadstuffs is as follows:† Mix 150 grams of fresh bread with 500 c.c. of water, add 100 c.c. of concentrated hydrochloric acid and boil for two hours connected with a reflex condenser.‡ Cool the resulting brown liquid to room temperature, filter with suction through a moistened fat-free paper, and wash with cold water. Dry the paper and residue for an hour at 100° to 110°, remove the residue as com-

* Bul. 67, Office of Experiment Stations, U. S. Dept. Agriculture.

† *Ztschr. angew. Chem.*, 1902, 121.

‡ In treating meal or flour, heat for an hour in a waterbath and then boil for an hour with the reflux condenser attached.

pletely as possible from the filter paper and grind it with sand in a mortar. Cut up and add the filter paper, and transfer the dry mixture to a paper extraction thimble and treat with ether or petroleum ether in an extractor.

Dormeyer's method,† designed originally for the determination of fat in animal tissues has been adapted to vegetable foods by Beger.† From 3 to 5 grams of substance are mixed with 480 c.c. of water, 20 c.c. of 25 per cent. hydrochloric acid, and one gram of fat-free pepsin. The mixture is kept at 37° to 40° for twenty-four hours, filtered with suction through a paper supported on a porcelain plate and covered with asbestos, and both the filtrate and the residue extracted with ether.

Determination of Nitrogen Compounds.

Determine total nitrogen as described in Chapter II. For the separation of proteid from non-protied nitrogen in cereals. Stutzer's cupric hydroxide method‡ has been most commonly used and is "official" for agricultural products. In examining wheat flour with reference to its baking qualities it is desirable to determine also the salt-soluble and the alcohol-soluble proteids using the methods recently adopted provisionally by the Official Agricultural Chemists.§

The extended investigations by Osborne and his associates ‖ and by Ritthausen ¶ have shown that nearly all of the cereal proteids contain over 16 per cent. of nitrogen so that the results obtained by multiplying the nitrogen by 6.25 are too high. The factors now regarded as most nearly correct are; for wheat, rye, and barley, 5.70 **; for maize, oats, rice, and buckwheat, 6.00. The old factor 6.25 is, however, still frequently used for the sake of uniformity or for comparison with earlier work. In reporting results, therefore, the factor used should always be given.

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* *Arch. f. ges. Physiol.* (*Pflüger*), 1895, 61, 341; 1896, 65, 90.

† *Chem. Ztg.*, 1902, 26, 112.

‡ Bul. 46, Bur. Chem., U. S. Dept. Agriculture.

§ Circular 20, Bur. Chem., U. S. Dept. Agriculture.

‖ Reports Conn. Agl. Expt. Station, 1890, *et seq.* Much of the work has also appeared in *Journ. Amer. Chem. Soc.*, *Amer. Chem. Journ.*, and *Amer. Journ. Physiol.*

¶ Summarized in *Landw. Vers. Stat.*, 1896, 47, 391.

** The factor 5.68 has recently been proposed for wheat flour.

Determination of Crude Fiber.*

Extract 2 grams of the substance with ordinary ether or use the residue from the determination of the ether extract. To this residue, in a 500 c.c. flask, add 200 c.c. of boiling 1.25 per cent. sulphuric acid; connect the flask with an inverted condenser, the tube of which passes only a short distance beyond the rubber stopper into the flask. Boil at once, and continue the boiling for thirty minutes. A blast of air conducted into the flask may serve to reduce the frothing of the liquid. Filter, wash with boiling water till the washings are no longer acid; rinse the substance back into the same flask with 200 c.c. of a boiling 1.25 per cent. solution of sodium hydroxide, practically free from sodium carbonate; boil at once, and continue the boiling for thirty minutes in the same manner as directed above for the treatment with acid. Filter on a Gooch crucible, and wash with boiling water till the washings are neutral; dry at 110°; weigh; incinerate completely. The loss of weight is crude fiber.

The filter used for the first filtration may be linen, one of the forms of glass wool or asbestos filters, or any other form that secures clear and reasonably rapid filtration. The solutions of sulphuric acid and sodium hydroxide are to be made up of the specified strength, determined accurately by titration and not merely from specific gravity.

Determination of Ash.

Char about 2 grams and burn to whiteness at the lowest possible red heat, preferably in a flat bottomed platinum dish in a muffle.

If considerable quantities of phosphates are present these may fuse over some of the carbon and render its combustion very slow. In such cases, extract the charred mass with a little hot acetic acid, set aside the solution till the char is burned, then evaporate it to dryness in the same dish and heat the residue to dull redness till the ash is white or nearly so. Samples containing added salt should be extracted with water before charring and the determination finished as just described. The precautions given in Chapter I. should always be observed.

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* Bul. 46, Bur. Chem., U. S. Dept. Agriculture. See also Thatcher: *Journ. Amer. Chem. Soc.*, 1902, 24, 1210; Browne: *Ibid.*, 1904, 25, 315.

Additional Tests and Determinations.

For discussions of tests for foreign substances present as adulterants the references given below should be consulted. Such adulteration of cereal products is not common in America. The determinations most often required, in addition to those already given are such as to show the usefulness of the material for some particular purpose. The value of wheat flour for breadmaking depends largely upon the proportion of alcohol-soluble proteid (gliadin) which it contains, and upon the acidity. The gliadin is most abundant in the interior of the wheat kernel and therefore in the highest commercial grades of flour. Acidity is objectionable both as an indication of deterioration and because it acts upon the gliadin injuring the physical properties which are especially important in breadmaking.

To determine acidity, shake 10 grams of the dry sample with 100 c.c. of cold water, filter, and titrate an aliquot part with tenth-normal sodium or potassium hydroxide using phenolphthalein as indicator. In fine flour the acidity calculated as lactic acid should not exceed 0.10 per cent.

Interpretation of Results.

*Official Definitions and Standards.**

1. *Grain* is the fully matured, clean, sound, air-dry seed of wheat, maize, rice, oats, rye, buckwheat, barley, sorghum, millet, or spelt.

2. *Meal* is the sound product made by grinding grain.

3. *Flour* is the fine, sound product made by bolting wheat meal and contains not more than 13.5 per cent. of moisture, not less than 1.25 per cent. of nitrogen, not more than 1.0 per cent. of ash, and not more than 0.50 per cent. of fiber.

4. *Graham flour* is unbolted wheat meal.

5. "*Whole wheat flour*," "*entire wheat flour*," improperly so called, is fine wheat meal from which a part of the bran has been removed.

6. *Gluten flour* is the product made from flour by the removal of starch and contains not less than 5.6 per cent. of nitrogen and not more than 10 per cent. of moisture.

7. *Maize meal, corn meal* or *Indian corn meal* is meal made from sound maize grain and contains not more than 14 per cent. of moisture, not less than 1.12 per cent. of nitrogen, and not more than 1.6 per cent of ash.

8. *Rice* is the hulled and polished grain of *Oryza sativa.*

9. *Oatmeal* is meal made from hulled oats, and contains not more

* Circular No. 13, Office of the Secretary, U. S. Dept. Agriculture.

than 8 per cent. of moisture, nor more than 1.5 per cent. of crude fiber, not less than 2.24 per cent. of nitrogen, and not more than 2.2 per cent. of ash.

10. *Rye flour* is the fine sound product made by bolting rye meal and contains not more than 13.5 per cent. of moisture, not less than 1.36 per cent. of nitrogen, and not more than 1.25 per cent. of ash.

11. *Buckwheat flour* is bolted buckwheat meal and contains not more than 12 per cent. of moisture, not less than 1.28 per cent. of nitrogen, and not more than 1.75 per cent. of ash.

Where percentages are given in these standards they are, of course, intended to represent normal limits rather than averages or extreme limits.

Composition of Entire Grains.

Wiley* estimates the approximate composition of average typical American grains as follows:

PERCENTAGE COMPOSITION OF ENTIRE GRAINS (WILEY).

	Barley.	Buck-wheat.	Maize.	Oats.	Rice unhulled.	Rye.	Wheat.
Moisture	10.85	12.00	10.75	10.00	10.50	10.50	10.60
Protein (Nitrogen × 6.25)	11.00	10.75	10.00	12.00	7.50	12.25	12.25
Fat (Ether Extract)	2.25	2.00	4.25	4.50	1.60	1.50	1.75
Crude Fiber	3.85	10.75	1.75	12.00	9.00	2.10	2.40
Ash	2.50	1.75	1.50	3.50	4.00	1.90	1.75
Carbohydrates (diff.)	69.45	62.75	71.75	58.00	67.40	71.75	71.25

Composition of Mill Products.

An extended study of the mill products of wheat made by Teller at the Arkansas Experiment Station, 1894 to 1898,† included a milling experiment in which the principal products of a long process (7 break) roller mill were analyzed with the following results:

PERCENTAGE COMPOSITION OF MILL PRODUCTS OF WHEAT (TELLER).

	Patent Flour.	Straight Flour.	Low Grade Flour.	Ship Stuff.	Bran.	Whole Wheat.	Pure Germ.
Moisture	13.75	13.90	13.22	12.25	12.85	13.90	6.80
Ash	.33	.47	.90	3.12	5.80	2.15	4.65
Crude Fiber	.17	.26	.74	3.55	6.14	2.17	1.60
Fat	1.05	1.25	1.70	4.80	5.20	2.15	14.38
Protein (Nitrogen × 5.7)	9.69	10.37	12.88	16.36	15.56	12.31	36.00
Carbohydrates (diff.)	75.01	73.75	70.56	59.02	54.45	63.32	36.55
Total Nitrogen	1.70	1.82	2.26	2.87	2.73	2.16	6.34
Proteid Nitrogen	1.65	1.72	2.20	2.68	2.51	1.98	
Amid Nitrogen	.05	.10	.06	.19	.22	.18	‡

* Bull. 45, Bur. Chem. U. S. Dept. Agriculture.

† Buls. 42 and 53, Ark. Expt. Station (Fayetteville, Ark.).

‡ The germ is richer in amid nitrogen than other parts of the wheat kernel.

Under the system of milling now practiced in the Northwest a number of "streams" of flour are produced which are afterward united in different proportions to form the market grades of flour. Snyder has recently published* analyses of the different "streams" as obtained in milling No. 1 Northern wheat by typical modern machinery. A sample of wheat containing 13.07 per cent. moisture and 2.28 per cent. nitrogen gave streams of flour containing from 9.01 to 11.68 per cent. moisture, and from 1.92 to 2.95 per cent. of nitrogen. The "gliadin number," or percentage of the total nitrogen existing in the form of alcohol-soluble proteids, varied from 39.51 to 66.67. It is interesting to note that some of the streams of flour thus obtained from average wheat in the ordinary milling process contain considerably more nitrogen than was recently found in the majority of so-called gluten and diabetic flours obtained in the market.†

For additional analyses and results of experiments upon the digestibility and nutritive value of cereal products see Bul. 13, Part 9, Bureau of Chemistry, and Buls. 28, 67, 85, 101, 126, and 143, Office of Experiment Stations, U. S. Department of Agriculture.

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* Bul. 85, Minn. Expt. Station, St. Anthony Park, Minn , 1904.

† Sherman and Burr: *New York Medical Journal*, 74, 686 (Oct. 12, 1901).

CHAPTER XIV.

Milk.

Cows' milk is concisely described as essentially an aqueous solution of milk sugar, albumin, and certain salts, holding in suspension globules of fat and in a state of semi-solution casein together with mineral matter (Richmond). Small amounts of other compounds are also present, but need not be considered here.

Standard milk (whole milk) is defined * as the lacteal secretion obtained by the complete milking of one or more healthy cows properly kept and fed, excluding that obtained within fifteen days before and five days after calving, and contains not less than 12 per cent. of total solids, not less than 8.5 per cent. of solids not fat, and not less than 3.25 per cent. of milk fat.

These limits are considerably below the average and considerably above the lowest authentic figures which have been found. Average milk may be assumed to contain 12.9 to 13 per cent. of total solids made up of: —

	Fat.	Protein.	Milk Sugar.†	Ash.
In round numbers‡	4.0	3.3	5.0	0.7
Estimated average	4.00	3.35	4.88	0.72

The protein content of average milk is, therefore, about one-fourth of the total solids. In general the same relation holds in milk which is richer than the average. Each increase of 1 per cent. in total solids thus involves on the average an increase of 0.25 per cent. of proteids, the remaining 0.75 per cent. being practically all fat. This increase in proteids and fat is usually accompanied by a slight increase in ash and decrease in milk sugar. The following average percentages illustrate these relations in rich milk: —

	Total Solids.	Fat.	Protein.	Milk Sugar.	Ash.
Average for 5 years; mixed evening milk of 400 to 500 cows	14.62	5.39	3.66	4.82	0.75
Average of 13 unusually rich samples from individual cows	18.03	7.76	4.68	4.76	0.83

* Circular No. 13, Office of the Secretary, U. S. Dept. Agriculture.

† The figures for milk sugar include the small amount of undetermined non-nitrogenous matter.

‡ These are the figures used in most publications of the U. S. Dept. Agriculture.

The composition of milk of less than average richness cannot be so definitely stated. In some cases there is a deficiency of fat and protein with no decrease in milk sugar, while in other cases the reverse is true. Usually if an unadulterated milk is poor in fat it will be found proportionately poor in protein, while if the fat is normal the protein is usually also normal and the low percentage of solids not fat is due to a deficiency in milk sugar.

Several hundred American analyses, made before 1890, compiled and averaged in ten groups arranged according to percentage of total solids, gave the following results.*

COOKE'S COMPILATION OF AMERICAN ANALYSES OF MILK.

Group No.	Total Solids. Per Cent.	Fat. Per Cent.	Proteids. Per Cent.	Sugar and Ash. Per Cent.	Group No.	Total Solids. Per Cent.	Fat. Per Cent.	Proteids. Per Cent.	Sugar and Ash. Per Cent.
1	11.35	3.20	2.99	5.16	6	13.71	4.46	3.48	5.77
2	11.77	3.36	3.03	5.38	7	14.25	4.87	3.65	5.73
3	12.21	3.60	3.10	5.51	8	14.77	5.20	3.87	5.70
4	12.75	3.82	3.29	5.64	9	15.17	5.47	4.07	5.63
5	13.17	4.09	3.40	5.68	10	15.83	5.88	4.26	5.69

As a rule the percentage of milk sugar and ash is most nearly constant, that of fat is most variable, while the protein varies with the fat, but to a much smaller extent. The variations which may be regarded as usual and the extreme variations which the writer has found authentically recorded are as follows:—

	Fat. Per Cent.	Solids Not Fat. Per Cent.	Proteids. Per Cent.	Milk Sugar. Per Cent.	Ash. Per Cent
Usual variations.....	3–6	8.5–9.5	3–4	4.6–5	0.7–0.78
Extreme variations†..	1.04–14.67	4.90–13.76	2.86–9.98	2.33–5.28	0.66–1.44

The extreme variations are of no practical value as a means of determining the limits within which milk shall be considered unadulterated, partly because it is possible to practice "adulteration through the cow" (*i. e.*, by selection, feeding, and manner of milking to obtain "genuine" milk much below the normal quality), but mainly because the milk which reaches market is practically always the mixed product of several cows so that individual variations have comparatively little effect.

There are many causes of variation in the composition of cow's milk. Only the most important can be given here. Other con-

* Cooke: Vermont Agricultural Experiment Station Report for 1890, p. 97.

† Including only results obtained from apparently healthy cows, believed to have been milked regularly under normal conditions.

ditions being normal the percentages of fat and proteids are higher in autumn and winter than in spring and summer; they also increase as the amount of milk decreases toward the end of each period of lactation. Milk drawn in the evening is generally 0.3 to 0.4 per cent. richer in fat than that obtained in the morning and at any one milking the last portions drawn are much richer than the first. The influence of a change of food upon the percentage composition of milk is usually only temporary. In general the peculiarities of breed * and the qualities of individual animals are the most important factors in determining the richness of milk. Aside from all these conditions the milk of individual cows is subject to considerable fluctuation, especially in fat content. Thus the analyses of 60 monthly samples of the mixed milk of about 500 cows showed a variation of 0.89 in the percentage of fat, the greatest deviation from the average being 0.50 per cent. About one-half of the determinations of fat in the milk of individual cows of the herd during the same period were more than 0.50 per cent. and about one-fifth were more than 1.0 per cent. above or below the average. Milk representing the mixed product of several farms, such as is now commonly sold in large cities, should, therefore, be much more uniform in composition than that of a single cow or a small herd.†

TAKING AND PRESERVATION OF SAMPLES.

If the lot of milk to be sampled is small it can be mixed by pouring from one vessel to another from two to ten times, according to the extent to which the cream has separated, and the portion for analysis dipped, or withdrawn by means of a pipette, from near the center. When the sample is too large to be handled in this way it should be transferred if necessary to a cylindrical can and sampled by means of a Scovell tube.‡ In order to obtain a

* For comparison of the milk of different breeds see Richmond's Dairy Chemistry, pp. 122–126, Report of the New York State Expt. Station for 1891 (abstracted in the Expt. Station Record, 4, 263), and Report of the Wisconsin Expt. Station for 1901, p. 85.

† Fuller discussions of the variations in the milk of individual cows and mixed milk of herds will be found in some of the reference books given at the end of the chapter, in the papers on the composition of milk published annually by Richmond in the *Analyst*, and in Hittcher's Gesammtbericht über die Untersuchung der Milch, Berlin, 1899.

‡ Wiley's Agricultural Analysis, Vol. III., p. 470, Leach's Food Inspection and Analysis, p. 95. These sampling tubes are sold by dealers in dairy apparatus.

proper sample of a large lot of milk delivered in cans of the same diameter, it is only necessary to sample each can with the Scovell tube and mix the portions thus obtained.

The sample should be placed at once in a clean, dry, sterile bottle, tightly stoppered, and analyzed as soon as possible. Before withdrawing each portion for analysis the sample must be thoroughly mixed by pouring — not by shaking.

If the analysis cannot be made at once or if the sample is to be kept for some time after the analysis, it must either be stored at a temperature near the freezing point or preserved by the addition of an antiseptic. Formaldehyde * added, while the milk is still fresh, in the proportion of 1 : 1000 will preserve the sample for months without apparent change. This amount of formaldehyde has a scarcely perceptible influence upon the analytical results. If preservation for only a few days is required a smaller amount of formaldehyde should be used, 1 : 2000 to 1 : 10,000 according to the freshness of the milk.

PRELIMINARY OR PARTIAL EXAMINATION.

Determination of Specific Gravity.

The specific gravity of milk is usually between 1.029 and 1.034. Since cream is considerably lighter than milk, the specific gravity would be lowered by the addition of water or of cream, but cases in which genuine milk shows a low specific gravity as a result of high fat content are very rare. As already explained, high percentages of fat are normally accompanied by high percentages of proteids, so that in most cases the specific gravity is higher in rich than in poor milk. With practice the samples which are exceptions to this rule can usually be detected by noticing the apparent viscosity and opacity of the milk as it runs from the surface of the lower bulb of the lactometer. The specific gravity taken in connection with this appearance is much used as a preliminary test by milk inspectors and is recommended by Richmond as the best means of rapidly testing each lot of milk received by a large dairy.

The Quevene, Veith, and Soxhlet lactometers are hydrometers of sufficient range for use with milk and so graduated as to read the "excess gravity" over water taken as 1000. Thus a milk of

* Other preservatives are sometimes useful. See Richmond's Dairy Chemistry, p. 144.

1.0315 specific gravity gives a lactometer reading of 31.5°. These instruments are often made to include a Fahrenheit thermometer, the scale of the latter being on the same stem with the lactometer scale. The lactometer reading should be taken between 50° and 65° F. and corrected for temperature by adding or subtracting 0.1° for each degree F. above or below 60. The New York Board of Health lactometer has a scale reading zero in pure water and 100 at 1.029 specific gravity. To convert the readings of this scale into the lactometer degrees described above, multiply by 0.29.

Volumetric Determination of Fat.

Babcock, in 1890, introduced the first satisfactory rapid method for the determination of fat in milk. On mixing milk with approximately an equal volume of strong sulphuric acid, the casein is dissolved while the fat remains unchanged and can be separated by centrifugal force. The test is performed in a bottle with a neck so graduated that the percentage of fat can be read off directly upon removing the bottle from the centrifuge.

Determination. — Measure 17.6 c.c. of milk at 14° to 18° (about 55° to 65° F.) and introduce into the test bottle. Add 17.5 c.c. of sulphuric acid of 1.82 sp. gr. (commercial concentrated acid is usually the right strength) allowing the acid to flow down the side of the bottle so as not to mix with the milk. When acid has been added to all of the bottles and everything is ready to start the whirling, mix the milk and acid quickly and thoroughly by shaking and continue the shaking until the curd is in solution and the liquid has reached a permanent and uniform color. Then place an even number of the bottles in opposite pockets in the machine and whirl at the rate of 800 to 1200 revolutions per minute, according to the diameter of the wheel which carries the bottle. After whirling five minutes, fill with hot water to the shoulder of the bottle and whirl two minutes, then fill with hot water to near the top of the graduation in the neck and whirl again for two minutes. The percentage of fat is now shown by the height of the column in the graduated neck of the bottle.

Notes. — The capacity of the graduated neck of the bottle from 0 to 10 is 2 c.c. It is assumed that the 17.6 c.c. of milk taken for the determination will weigh ten times as much as 2 c.c. of warm butter fat. It is important that the final readings be taken while the fat is still warm. On account of the unavoidable contraction

of the fat while taking these readings it is customary to read from the bottom of the lower to the top of the upper meniscus. The result is usually within 0.2 per cent. of that found by the gravimetric method. The column of fat should be of a clear yellow color throughout. If the acid used is too weak, flocks of undissolved casein are apt to be found in the lower part of the fat column; if too strong the acid may char the fat. For a full discussion of the details of the test with directions for applying it to other dairy products see the work of Farrington and Woll.*

The most important modifications of the Babcock method are fully described in Richmond's Dairy Chemistry, pp. 174–192.

Calculation of Solids from Specific Gravity and Fat.

Many formulæ have been proposed by which to calculate the percentage of solids in milk from the percentage of fat and the specific gravity. The results thus obtained are sufficiently accurate for many technical purposes and often for routine inspection work which is not to be made the basis of legal action. Such formulæ may be found in many of the works referred to at the end of this chapter. They are necessarily based on the assumption that each per cent. of fat causes a definite decrease, and each per cent. of solids not fat a definite increase, in the specific gravity.

Since the solution densities of proteids, milk sugar, and milk ash differ considerably † any change in the relative proportions of these constituents must alter the solution density of the solids not fat and thus diminish the accuracy of this method.

One of the simplest of these formulæ is that of Richmond:

$$\text{Total solids} = \frac{\text{Lactometer reading}}{4} + 1.2 \text{ fat} + 0.14.$$

With samples which do not differ greatly from the average composition the results thus calculated are usually accurate within 0.25 per cent.

DETERMINATION OF FAT, PROTEIDS, MILK SUGAR, AND ASH.

Total Solids and Ash.

Into an accurately weighed flat-bottomed platinum dish introduce two to five grams (depending upon the size of the dish; see

* Testing Milk and Its Products. Madison, Wisconsin, 1899.

† Allen: Commercial Organic Analysis, Vol. IV., p. 166.

below) of the thoroughly mixed milk and weigh quickly to the nearest milligram. If this weighing cannot be accomplished within one minute the dish should be covered with a weighed watch glass to retard evaporation. Place the open dish on a water bath or on top of the boiling water oven until nearly all of the water is expelled; dry to constant weight in a boiling water oven or an air bath kept constantly at 97° to 100°. The residue is somewhat hydroscopic and must be weighed quickly upon removal from the desiccator in order to obtain the correct amount of total solids.

Ignite the dry solids in a muffle at 550° to 600°, or, if this is not feasible, regulate a Bunsen burner to give a very small colorless flame and apply this carefully with constant attention so that no part of the dish is heated above the lowest possible redness. The ash should be white or very light gray. After obtaining the weight of the ash it may be used in testing for preservatives, as described below.

Notes on Total Solids. — When the same portion is not to be used for the determination of ash a platinum dish is not essential. Lead foil bottle caps are then very convenient, as they are easily numbered by scratching, quickly heated and cooled, and so cheap that each dish can be rejected after being used once. In order that a larger surface may be exposed, the dish may contain dry sand or other porous material and a small stirring rod, weighed with the dish and used to stir the residue while drying. Unless absorbed upon porous material, no more than 0.5 gram of milk for each square centimeter of the area of the bottom of the dish should be taken for the determination.

The methods used in the Government Laboratory, London, for the determination of solids in sour or fermented milk and the estimation of the solids lost in fermentation have recently been described by Thorpe.*

Notes on Ash. — Normally about two-thirds of the ash of cows' milk is insoluble in hot water. The presence of a larger proportion of soluble ash may be due to the use of mineral preservatives or to the addition of salts to restore the density and ash content to milk which has been watered. Special tests for some of the mineral preservatives are given beyond. In important cases it may be necessary to analyze the ash to show whether it is of normal char-

* *Journ. Chem. Soc.*, 1905, 87, 206.

acter. Richmond * gives the following as the average composition of milk ash: Calcium oxide, 20.27 per cent.; magnesium oxide, 2.80 per cent.; potassium oxide, 28.71 per cent.; sodium oxide, 6.67 per cent.; phosphoric anhydride, 29.33 per cent.; chlorine, 14.00 per cent.; carbonic anhydride, 0.97 per cent.; sulphuric anhydride, trace; ferric oxide, etc., 0 40 per cent. According to most other writers † milk ash contains sulphates, but only traces of carbonates. A sample of ash from the mixed milk of about 500 cows which has been partially examined by Thompson and the writer, shows no appreciable amount of carbonates and only traces of sulphates. The ash was prepared at known temperatures with the precautions given in Chapter I. According to the results thus far obtained there was no volatilization of chlorides below 650°, but even at 450° to 500° there was considerable loss of chlorine due doubtless to the formation of acid products in the combustion of the organic constituents of the milk.

Fat. — Gravimetric Determination.

Adams' Paper Coil Method.

In this method the milk is dried on porous paper, the fat extracted by means of ether into a weighed flask, the ether evaporated, and the fat weighed.

Apparatus. — (1) Strips of thick absorbent fat-free paper about 55 cm. long and 6.25 cm. wide,‡ each rolled into a loose coil and fastened by means of a piece of wire or fat-free thread. If difficulty is found in making a loose coil, two pieces of fat-free string may be laid lengthwise upon the paper strip before rolling it up. This, however, should not be necessary.

(2) A Soxhlet apparatus for ether extraction; the form having ground glass connections being recommended.

(3) A safety water bath or, preferably, an electric heater which can be easily regulated.

Determination. — Mix the milk thoroughly and absorb a known amount, about 5 grams, on the paper coil. The milk can be measured by means of a 5 c.c. pipette and delivered directly upon the

* Dairy Chemistry, p. 32.

† See tabulated analyses in Stohmann's Milch- und Molkereiproducte, p. 89.

‡ Strips of paper especially prepared for this purpose are made by Schleicher and Schüll. If these are not available the paper strips must be very carefully extracted before use. See Richmond's Dairy Chemistry, pp. 91–93.

coil, but as milk is more viscous than water an ordinary 5 c.c. pipette will deliver less than 5 c.c. of milk, so that this method can be made accurate only by determining experimentally the amount of milk which the pipette actually delivers. A better method is to pour about 5 c.c. into a very small beaker, weigh quickly to centigrams and at once absorb the milk by standing the coil in the beaker. The absorption can be hastened by inclining the beaker and rotating the coil. The last drops in the beaker must be carefully absorbed. Stand the coil upon the dry end and re-weigh the beaker quickly to centigrams. If carried out rapidly this method is considerably more accurate than measuring with a pipette. Dry the coil thoroughly in a boiling water oven, place in a Soxhlet extractor, and extract with anhydrous ether, using the electric heater or safety water bath and keeping the apparatus as far as possible from free flames. If not more than 5 grams of milk is used and the extractor siphons at intervals of 10 to 15 minutes, the extraction need not be continued longer than three hours. At the end of the extraction disconnect the apparatus, remove the coil, replace the extractor, recover nearly all the ether by allowing it to collect in the space formerly occupied by the coil, return the ether to its bottle, and heat the flask containing the fat in a boiling water oven until the weight is practically constant.

Notes. — As the milk is absorbed by the paper the greater part of the fat is left on or near the surface, so that it is very rapidly extracted by the ether. The coil must be thoroughly dried before extracting with ether. The drying can be hastened by pressing in the dry end of the coil so that the inner layers of the wet end are made to project in the form of a cone. Such a coil will usually be dry after standing two to three hours in the boiling water oven. On removing from the oven press back the projecting end of the coil and place it, milk end down, in the extractor; connect with the flask, pour in ether until it siphons into the flask, then enough more ether to cover about half of the coil. This is sufficient to avoid any danger of the flask going dry during the extraction, if the heat is so regulated that no perceptible amount of ether escapes through the reflux condenser. To dry the extract leave it in the boiling water oven for three hours, allow to cool for one-half hour, weigh, and then repeat, heating about one hour each time, until two successive weighings show a loss of less than one milligram. In laboratories where many determinations are made it is cus-

tomary to dry the extract for a fixed length of time (usually five hours), which has been found by experience to be sufficient.

*Babcock Asbestos Method.**

Provide a hollow cylinder of perforated sheet metal, 60 mm. long and 20 mm. in diameter, closed 5 mm. from one end by a disk of the same material. The perforations should be about 0.7 mm. in diameter and about 0.7 mm. apart. Fill loosely with from 1.5 to 2.5 grams of freshly ignited, woolly asbestos, free from fine and brittle material, cool in a desiccator, and weigh. Introduce a weighed quantity of milk (between 3 and 5 grams) and dry at 100° to constant weight. This weight shows the percentage of total solids. Place the cylinder in an extractor and complete the determination of fat as described above.

This method avoids the possibility of having any ether-soluble matter in the porous substance used to absorb the milk. It is especially recommended for the determination of fat in cream which cannot be absorbed upon the paper coil without previous dilution.

PROTEIDS.

Formerly milk proteids were precipitated, or the milk evaporated to dryness, and the residue after washing with ether and dilute alcohol was dried, weighed, burned, and the ash deducted. On account of the difficulty of completely removing the sugar and fat, the results thus obtained were usually too high; so that in the older statements of the composition of milk (some of which are still often quoted) the proteids were usually overestimated.

Protein in milk is now calculated from the nitrogen content, multiplying the latter by the usual factor 6.25 or sometimes by a special factor, 6.33 or 6.37, based on analyses of milk proteids showing less than 16 per cent. of nitrogen.

To determine the total nitrogen in milk pour 5 to 10 grams of the sample into a small beaker, weigh quickly to centigrams, pour the milk carefully into a Kjeldahl flask, re-weigh the beaker, and introduce 20 to 25 c.c. of concentrated sulphuric acid into the flask in such a way as to wash down any milk which may have remained in the neck. Add 0.7 gram of mercury, heat gently over a very small flame until most of the water is expelled and no more frothing or spirting occurs, then increase the size of the flame and complete the determination as described in Chapter II.

* Bul. 46, Bur. Chem., U. S. Dept. Agriculture.

Casein can be precipitated by acidulating the milk or by means of magnesium sulphate. Determination of nitrogen in the washed precipitate shows the amount of casein in the milk. Albumin can be precipitated by boiling the filtrate and determined in the same manner. Detailed directions for these determinations will be found in Bulletin 46, Bureau of Chemistry, U. S. Dept. Agriculture.

Milk Sugar or Lactose.

In most cases the direct determination of lactose is unnecessary as the difference between the percentage of total solids and the sum of the percentages of fat, proteids, and ash should not differ from the true percentage of lactose by more than 0.1 to 0.2 per cent. When direct determination is desired either the polariscopic method or one of the methods based upon the reduction of copper can be used. In the former case the proteids are precipitated and the solution clarified by means of mercuric nitrate or iodide, in the latter by cupric hydroxide or acetic acid, alum, and aluminum hydroxide.

*Optical Determination.**

Place 65.8 grams of milk in each of two flasks, one graduated at 100, the other at 200 c.c., to each add 4 c.c. of mercuric nitrate solution,† fill to the mark, shake, filter through dry paper, and polarize in a 200 mm. tube in the Schmidt and Haensch polariscope.

In each case the reading is too high on account of the volume occupied by the precipitate which contains the proteids and fat of the milk. This volume is twice as great in proportion in the 100 c.c. as in the 200 c.c. flask. The corrected reading and the volume occupied by the precipitate can, therefore, be calculated by the method of double dilution as in the following example: —‡

Weight of milk taken 65.8 grams, or twice the "lactose normal" weight§ for the Ventzke scale.

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* Wiley and Ewell: *Journ. Amer. Chem. Soc.*, 1896, 18, 428.

† To prepare this solution dissolve mercury in twice its volume of nitric acid, 1.42 specific gravity, and add to the solution an equal volume of water; or prepare a solution of equal strength by dissolving solid mercuric nitrate in water acidulated with nitric acid.

‡ Compare Wiley's Agricultural Analysis, Vol. III., pp. 102, 278.

§ Calculated from the sucrose normal weight and the approximate specific rotatory powers of sucrose and lactose. These data and directions for the manipulation of the polariscope have been given in Chapters V. and VI.

Average reading from 100 c.c. flask, 10.45.
" " " 200 c.c. " 5.075.

Then

10.45 — (5.075 × 2) = 0.30 (half the error in the higher reading).
10.45 — (0.30 × 2) = 9.85 (corrected reading for 100 c.c. flask).
9.85 ÷ 2 = 4.925, corrected percentage of lactose.

The volume of the precipitate is calculated as follows:

10.45 ÷ 2 = 5.225, apparent percentage of lactose (100 c.c. flask).

Then

$$5.225 : 4.925 :: 100 : x.$$

$x = 94.26$, the volume of solution in the 100 c.c. flask. Hence the volume of the precipitate is 5.74 c.c.

*Determination by Fehling Solution.**

Dilute 25 c.c. of milk with 400 c.c. of water in a 500 c.c. flask, add 10 c.c. of the copper sulphate solution used in the Fehling method, mix and add 4.4 c.c. of normal sodium or potassium hydroxide (or an equivalent amount of a weaker standard solution), fill to the mark, mix, and filter through dry paper. The filtrate must contain copper in order to ensure the absence of any trace of free alkali. In this clear filtrate lactose can be determined by means of Fehling solution either by Defren's method as described in Chapter V., or by Soxhlet's method, Bul. 46, *l. c.* The milk is so greatly diluted in clarifying the solution that the volume of the precipitated proteids and fat can be neglected.

If lactose is to be determined volumetrically, the proteids can be precipitated and the solution clarified as described in Richards and Woodman's Air, Water, and Food.

INTERPRETATION OF RESULTS.

The principal adulterations affecting the percentages of nutrients in milk are the addition of water (sometimes containing dissolved solids) and the removal of cream. These adulterations are sometimes difficult to detect with certainty because genuine cows' milk varies considerably both in fat and in other solids. Since the percentage of fat is more variable than that of solids not fat, skimming is more difficult to detect than watering. If as much as one-fourth of the fat were removed, the skimming would usually be in-

* Bul. 46, *loc. cit.*

dicated by the disturbance of the normal relation between the percentage of fat and that of proteids or of solids not fat, but the analysis cannot be said to prove the removal of cream unless it shows a lower percentage of fat than is ever found in genuine normal milk. Starting with average milk containing 4 per cent. fat and 9 per cent. solids not fat, one-tenth of the fat could be removed by skimming and the resulting product containing 3.6 per cent. fat could not be distinguished by analysis from genuine milk, while if the fat were reduced to 3.6 per cent. by watering, the solids not fat would be reduced to 8.1 per cent. which is sufficiently below the normal to be detected without difficulty. Occasionally genuine milk contains even less than 8.0 per cent. of solids not fat (the deficiency in most of these cases falling mainly upon the milk sugar) so that the limit of 8.5 for solids not fat might indicate watering where none had been practiced. Such errors are avoided by taking account of the proteids and ash. Milk should contain not less than 8.5 per cent. of solids not fat, 3.0 per cent. of proteids, 0.7 per cent. of total ash, 0.5 per cent. of ash insoluble in hot water. These four determinations will usually suffice to show whether the milk is genuine or has been watered with or without the addition of soluble solids.

UNITED STATES AND STATE STANDARDS FOR MILK, 1905.

	Total Solids, Per Cent.	Solids not Fat, Per Cent.	Fat, Per Cent.		Total Solids, Per Cent.	Solids not Fat, Per Cent.	Fat, Per Cent.
U. S. Dept. Agric...	12	8.5	3.25	New York.....	12	.....	3
District of Columbia.....		9	3.5	North Carolina.....	12	8.5	3.25
Georgia	.....	8.5	3.5	North Dakota.....	12	.....	3
Idaho	.....	8	3	Ohio	12	.....	3
Illinois	.....	.....	3	" May-June....	11.5	.....	.....
Indiana.....	.....	9	3	Oregon	12	9	3
Iowa.....	12.5	.....	3	Pennsylvania	12	.....	3
Kentucky	12	.....	3	Porto Rico	12	.....	3
Maine	12	.....	3	Rhode Island.....	12	.....	2.5
Maryland	12.5	.....	3.5	South Carolina.....	.....	8.5	3
Massachusetts	13	9.3	3.7	South Dakota.....	13	.....	3
" Apr.-Sept.	12	9	3	Utah	12.5	.....	3
Michigan.....	12.5	.....	3	Vermont.....	12.5	9.25	.....
Minnesota.....	13	.....	3.5	" May-June.	12	.....	.....
Montana	11.5	.....	3	Washington	.....	8	3
New Hampshire....	13	9.5	3.5	Wisconsin.....	.....	.....	3
" Apr.-Sept.	12	.....	3	Wyoming	12	.....	2.4
New Jersey.....	12	.....	.....	" May-June..	11.5	.....	.....

In most cases it is not necessary to show conclusively whether milk has been skimmed or watered, but only whether it meets the

requirements of a legal or trade standard. The principal standards in force in the United States on April 1, 1905, are given in the accompanying table from Circular No. 74, Bureau of Animal Industry, U. S. Dept. Agriculture.

PRESERVATIVES AND PRODUCTS OF FERMENTATION.

Only a few of the many products produced by the action of micro-organisms in milk and of the substances used to retard the formation of such products or to hide their presence can be considered in this chapter.*

FORMALDEHYDE.

Detection.

Of the many methods available for the detection of formaldehyde in milk only three of the best known and most delicate will be given.

Sulphuric Acid Test.†—Dilute 2 to 3 c.c. of milk with an equal volume of water in a test tube, add carefully so as not to mix the layers from 3 to 5 c.c. of concentrated commercial sulphuric acid or pure acid to which a trace of ferric salt has been added. If formaldehyde is present a violet ring forms at the junction of the two liquids. The charring of the milk by the sulphuric acid, makes it difficult to define the delicacy of the test. One part of formaldehyde in 100,000 of milk can be detected if the milk is fresh and the test is applied soon after adding the preservative.

Hydrochloric Acid Test.‡—Mix 10 c.c. of milk and 10 c.c. of concentrated hydrochloric acid containing about 2 mgs. of ferric chloride and heat slowly nearly to boiling, rotating the mixture occasionally to ensure solution of the curd. In the presence of formaldehyde a violet color develops, otherwise the solution slowly turns brown. The test is best performed in a porcelain casserole and in case of doubt the violet color is made much more distinct by adding 50 to 75 c.c. of water after having heated just below boiling for about a minute. The liquid must be observed

* Trade names and analyses of many proprietary preservatives will be found in the Year-Book of the U. S. Department of Agriculture for 1900, Chapin's Theory and Practice of Infant Feeding, and the *Zeitschrift für die Untersuchung der Nahrungs- und Genussmittel.*

† Hehner: *Analyst*, 1896, 21, 95.

‡ Leach: Ann. Rpts. Mass. State Board of Health, 1897, 558; 1899, 699; Food Inspection and Analysis, p. 140. See also Chapter IV.

carefully at the moment of dilution as the color which is brought out in this way fades very rapidly. This test is delicate to 1 : 250,000 but formaldehyde added to milk in such small quantities soon disappears. When added to the extent of 1 : 50,000 to 1 : 100,000 the presence of formaldehyde in the milk will be shown by this test for from 1 to 5 days.* In testing sour or stale milk the brown color noted above will often obscure the reaction given by a small amount of formaldehyde until the solution is diluted with water, but at this point the violet color can be seen even though the milk may have been much charred by the acid.

Gallic Acid Test. — This test has been described in Chapter V. To apply it to milk, acidulate 30 c.c. with 2 c.c. of normal sulphuric acid and distil. To the first 5 c.c. of distillate add 0.2 to 0.3 c.c. of a saturated solution of gallic acid in pure alcohol, incline the test tube and pour in slowly 3 to 5 c.c. of concentrated sulphuric acid. The presence of formaldehyde is shown by the characteristic blue ring described in detail in Chapter V. In the writer's experience this test is at least twice as delicate as either the sulphuric or the hydrochloric acid test. The latter would be sufficiently delicate for all practical purposes if milk samples could always be tested while fresh, but when small amounts of formaldehyde have been added one or two days previously, the gallic acid test may show the preservative where either of the other tests would fail. This gallic acid reaction may also be used very satisfactorily as a means of confirming any doubtful results obtained by either of the preceding tests as there is little danger of interference due to charring or to the appearance of other colors.

Determination.

Very small amounts of formaldehyde in milk can be determined by the following method, which is essentially that of Smith,† except that a larger quantity of sample is used.

To 300 c.c. of milk in a round-bottomed flask of about one liter capacity add 3 c.c. of (1 : 3) sulphuric acid and some glass beads to prevent bumping, heat gradually to boiling, preferably by means of a small rose-top burner, and distil until the distillate measures 60 c.c. Transfer this to a 100 c.c. flask, add 10 c.c. of standard

* Rivas: *University of Pennsylvania Medical Bulletin*, 1904, 17, 175. Unpublished experiments by Williams and the writer.

† *Journ. Amer. Chem. Soc.*, 1903, 25, 1036.

potassium cyanide solution, approximately tenth-normal, and mix; add a mixture of 15 c.c. of tenth-normal silver nitrate and 6 to 8 drops of 50 per cent. nitric acid, fill to the mark, shake, and filter through dry paper. Determine the excess of silver by the Volhard method and calculate the results as explained in Chapter V. under the description of the cyanide method as used for commercial solutions of formaldehyde. The precautions and the directions for standardizing there given should also be noted.

By this method from 32 to 39 per cent. of the formaldehyde in the milk is recovered and determined in the distillate. Assuming that the amount recovered represents 35 per cent. of the quantity in the milk, the latter can be estimated with a probable error of about one-tenth. Using this as a means of studying the disappearance of formaldehyde in milk, it was found in a typical experiment in which the proportion added was 1 : 40,000, that nearly three-fourths of the preservative had disappeared after two days at room temperature. After four days no formaldehyde was shown by this method but the violet color on dilution with water after heating with hydrochloric acid containing ferric chloride was unmistakable. The latter reaction could still be obtained after the mixture had stood for two weeks. When formaldehyde is added to milk in large proportion, 1 : 1000 to 1 : 10,000 as in the preservation of samples for analysis or reference, the rate of disappearance is much slower.

Hydrogen Peroxide.

Detection.

Hydrogen peroxide in uncooked milk is easily detected by adding to 10 to 15 c.c. of the milk, 2 to 3 drops of a 2 per cent. aqueous solution of paraphenylenediamine hydrochloride. In the presence of hydrogen peroxide a blue color appears either immediately upon shaking or after a few minutes depending upon the amount present. The reaction depends upon the action of an oxidizing enzyme in the milk and the condition of the milk, therefore, affects the delicacy of the test. According to Arnold and Mentzel * 1 part in 40,000 can be detected. Under ordinary conditions the delicacy is probably somewhat less than this. In comparative tests made immediately after adding the same amounts of

* *Ztschr. Unters. Nahr.-Genussm.*, 1903, 6, 306.

peroxide to sweet milks 1 to 2 days old and to very sour curdled milks 3 to 4 days old, the former were found to give the reaction much more strongly than the latter. In practice, however, the preservative would be added while the milk was sweet and would probably disappear entirely before the occurrence of curdling. Milk which has been boiled can be tested after adding an equal volume of fresh milk known to be free from peroxide.

Determination.

Chick,* in an investigation of the germicidal properties and rate of disappearance of hydrogen peroxide in milk, used a method based upon the titration of the iodine liberated by the peroxide on adding potassium iodide and sulphuric acid.

$$2KI + H_2O_2 + H_2SO_4 = K_2SO_4 + I_2 + H_2O.$$

Mettler† has used the method with satisfactory results in the following modified form: To 40 c.c. of water, 0.5 gram of potassium iodide, and 10 c.c. of 12 per cent. sulphuric acid in a glass-stoppered flask, add 10 c.c of the milk, stopper tight and allow to stand in a cool dark place for two and one-half hours. In order to guard against any possible loss of iodine during this time, use a flask with flaring mouth as described in connection with the determination of the iodine number (Chapter IX.), and fill the gutter around the stopper with a solution of potassium iodide. Finally titrate the iodine which has has been set free in the milk, using a fiftieth-normal solution of sodium thiosulphate. In this titration it is not necessary to use starch as indicator since the disappearance of the yellow color produced by the action of the iodine upon the proteids affords a satisfactory end point. Test analyses gave results about 3 per cent. too low, doubtless because of the absorption of iodine by the milk fat. This source of error can be avoided by curdling the milk with acid, filtering, and adding the iodide to a measured amount of filtrate; but this is considered inadvisable in view of the fact that the peroxide may be undergoing decomposition during the filtration.

SALICYLIC ACID AND SALICYLATES.

Hahn,‡ in experiments upon some of the methods most commonly recommended for the extraction of salicylic acid from foods,

* *Centralblatt für Bacteriologie und Parasitenkunde*, II. Abth., 1901, 1, 705.

† Thesis for the degree of Bachelor of Science, Columbia University, 1905.

‡ Thesis for the degree of Bachelor of Science, Columbia University, 1905.

recovered only a small percentage of the amount known to be present in milk. Separation of salicylic acid by distillation with steam is extremely slow, and extraction by shaking with ether or chloroform after precipitating the proteids by mercuric nitrate, is usually very incomplete. Better results can be obtained by the following modification of Remont's method: Acidulate 10 c.c. of milk with sulphuric or phosphoric acid, shaking well to break up the curd; add 10 c.c. of ether, mix by shaking gently so as not to form an emulsion, cork, and allow to stand in a cylinder or large test tube until most of the ether has separated. Draw off 5 c.c. of the ether layer, evaporate to dryness, boil the residue with 10 c.c. of 40 per cent. alcohol, cool, filter through dry paper if necessary to remove fat, and test 5 c.c. of the filtrate by adding 1 c.c. of 2 per cent. solution of ferric chloride. A purple or violet color is produced if salicylic acid is present. On standing the color fades somewhat and becomes pinkish.

Boric Acid and Borates.

In routine work * the ash obtained in the usual course of analysis is treated with two drops of dilute hydrochloric acid † and about a cubic centimeter of water. A strip of turmeric paper is then placed in the dish, allowed to soak for a minute, removed and allowed to dry in the air. A deep red color changing to green or blue when treated with dilute alkali shows the presence of boric acid. According to Leach this reaction is delicate to 1 part in 8000. The well-known flame test with methyl alcohol is less delicate but can be used in confirmation.

The turmeric test is very satisfactory for the detection of boric acid in the ash, but since a considerable loss of boron may occur in burning off the organic solids of milk, it is better in all important cases to take a separate portion for this test and make it strongly alkaline with sodium or calcium hydroxide before evaporating to dryness. All of the boric acid then remains in the ash and can be determined quantitatively by Thomson's method.‡

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* Leach: Food Inspection and Analysis, p. 144.

† Care should be taken to note whether any effervescence occurs. See carbonates and bicarbonates beyond.

‡ Glasgow City Anal. Soc. Reports, 1895; *Analyst*, 1896, **21**, 64; Sutton's Volumetric Analysis, 8th Ed., p. 100, 9th Ed., p. 98; U. S. Dept. Agriculture, Bur. Chem., Bul. 65, p. 110. The standard alkali used in the final titration should be freshly standardized against boric acid.

Fluorides.

If milk containing a small amount of fluoride is evaporated and the solids burned to ash in the usual way the fluorine is likely to be almost entirely lost. In the presence of a considerable excess of alkali this loss of fluorine does not occur.

To detect or determine fluorides, add 1 gram of sodium carbonate to 100 c.c. of milk, evaporate, and burn to ash. If only qualitative results are required, examine for fluorides by the well-known etching test on glass. For a quantitative determination of the fluorine, leach the mixture of ash and sodium carbonate thoroughly with hot water, nearly neutralize with sulphuric acid, leaving the solution slightly alkaline, and then apply Rose's method as modified by Treadwell and Koch: *Ztschr. anal. Chem.*, 1904, 43, 469.

Carbonates and Bicarbonates.

When milk contains the equivalent of 0.05 per cent. of sodium carbonate the ash obtained by direct ignition of the solids shows effervescence on addition of hydrochloric acid. Such effervescence is rarely if ever seen in the ash of pure milk, but since Richmond has found small amounts of carbonic acid in the ash of milk believed to have been pure,* the presence of carbonate or bicarbonate should be confirmed by applying Schmidt's test, in which 10 c.c. of milk are mixed with an equal volume of alcohol and a few drops of a 1 per cent. solution of rosolic acid. The color is brownish-yellow in pure milk but rose red in milk containing carbonate or bicarbonate. A comparative test with pure milk should always be made. The reaction is nearly as delicate as the test for effervescence in the ash.

Carbonates and bicarbonates are not to be regarded as preservatives, but as adulterants added to hide the presence of acid and thus give the milk a fraudulent appearance of freshness.

Acidity.

To determine the total acidity of milk, dilute 10 c.c. of sample with 90 c.c. of water and titrate with tenth-normal sodium or potassium hydroxide using phenolphthalein as indicator. The acidity is usually considered to be due mainly to lactic and car-

* The use of salicylates or other alkali salts of organic acids as preservatives may also give rise to carbonates in the ash.

bonic acids. In order to eliminate the carbonic acid, the mixture of milk and water may be boiled in a beaker loosely covered with a watch glass for ten minutes. Both the total acidity and the acidity after boiling are often calculated as due to lactic acid. The results are also frequently given as "degrees of acidity." This term unfortunately has no definite meaning when applied to milk and must be explained in each case. It is, therefore, recommended that results be expressed as "total acidity equivalent to per cent. of lactic acid" and "acidity after boiling equivalent to per cent. of lactic acid."

In a very recent paper * Thorpe recommends that the volatile acids be calculated as acetic acid and determined as follows: To 10 grams of milk in a platinum dish, add a little phenolphthalein and one-half the volume of tenth-normal sodium hydroxide which would be required to neutralize the total acidity. Evaporate to dryness on a water bath with frequent stirring, add 20 c.c. of boiling distilled water, stir thoroughly to disintegrate and detach the milk solids from the dish, and titrate with tenth-normal sodium hydroxide. The difference between the total volume of alkali used in this determination and the volume required to neutralize 10 grams of the original milk gives a measure of the volatile acids in the sample.

The causes and significance of the acidity of milk have been studied recently by Touchat,† Vieth and Siegfeld,‡ Richmond and Harrison, § Kirsten, || and Haune. ¶

Ammonia.

The Boussingault-Shaffer method for the determination of ammonia in urine ** has been thoroughly studied by Berg †† with regard to its applicability to the much smaller amounts of ammonia which occur in milk. The following is an outline of the method as adapted to milk: —

* *Journ. Chem. Soc.*, 1905, 87, 220.

† *British Food Journ.*, 1899, 199; Abs. *Jour. Chem. Soc.*, 1900, 78, ii, 582.

‡ *Milch Ztg.*, 29, 593; Abs. *Jahr. Thierchem.*, 1900, 261.

§ *Analyst*, 1900, 25, 120.

|| *Ztschr. Unters. Nahr.-Genussm.*, 1902, 5, 97.

¶ *Milch Ztg.*, 1904, 33, 659, 679, 709, 725; Abs. *Experiment Station Record*, 1905, 16, 595.

** Shaffer: *Amer. Journ. Physiol.*, 1903, 8, 330.

†† Thesis for the degree of Bachelor of Science, Columbia University, 1904.

Fifty c.c. of the sample are mixed, in a two-liter round-bottomed flask, with an equal volume of methyl alcohol, 10 grams of sodium chloride, and 0.5 gram of sodium carbonate. The latter liberates the ammonia from its salts, the salt diminishes the dissociation of the carbonate and thus prevents or retards the cleavage of ammonia from the nitrogenous organic compounds in the milk, and the alcohol also tends to prevent cleavage both by diminishing dissociation and by lowering the boiling point of the mixture. The flask is closed with a stopper having an inlet tube to provide for the admission of air and an outlet fitted with a distilling head and connected with two condensing cylinders (in series) containing together from 15 to 25 c.c. of twentieth-normal acid diluted with water to 40 c.c. The cylinders are connected with a suction pump. By this arrangement it is possible to distil the ammonia into the absorption cylinders completely within fifteen minutes at a temperature not above 60°.

Fresh milk of good quality yields less than 0.001 per cent. of ammonia when treated by this method. If the sodium chloride is omitted in the distillation a larger amount of ammonia is obtained. For convenience the ammonia thus easily split off from organic matter by dilute sodium carbonate at 55° to 60° is called "cleavage ammonia." Both the ammonia existing as such in the milk and the "cleavage ammonia" increase rapidly under conditions which favor the decomposition of proteids by bacteria or molds, and it is believed that these determinations will prove useful in the sanitary examination of milk. The methods and results are more fully discussed in a paper on the determination of ammonia in milk in the *Journal of the American Chemical Society* for February, 1905.

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ABSTRACTS.

ANALYTICAL CHEMISTRY.

BY ELWYN WALLER.

Testing Glass Vessels for Neutrality. Baroni (*Giom. Farm. Chim.*, LIII., 481). Fill three vessels respectively with 1 per cent. morphine hydrochloride, 0.5 per cent. strychnine hydrochloride and 1 per cent. $HgCl_2$, and then heat them half an hour in an autoclave at 112° C. If, by that time, any of the solutions show colored deposits the glass is not neutral.

Reducing Agent. Chapman (*Analyst*, XXIX., 346). Palladium-hydrogen is thoroughly satisfactory in many cases. A piece of Pd foil of such thickness that 2 inches square weighs 8 gms. is soldered to a stout Pd wire, and this is then made the negative electrode in a cell containing dilute H_2SO_4. After washing the metal is suspended in the boiling solution which it is intended to reduce, -ic salts of Fe and Cr as well as Ce are completely reduced. Those of Cu, Sn, As, Mn, Vd and Mo are only imperfectly reduced. $KClO_3$ was partially reduced — the corresponding Br and I compounds were not affected.

Diphenylamine as a Reagent for nitrates, etc. Alvarez (*Chem. News*, XCI., 155). Alone, diphenylamine produces a series of colors, succeeding each other rapidly. In conjunction with resorcin or beta naphthol more satisfactory and characteristic indications are obtained. Freshly prepare a solution of 10 c.c. H_2SO_4 containing 0.1 gm. pure diphenylamine and 0.1 gm. resublimed resorcin.

Five or six dops of this solution added to a few drops of solution containing 0.001 gm. of the salts tested on white porcelain. It gave:

With *nitrates*, permanent yellowish green, the edges becoming blue. Addition of alcohol afforded an orange liquid.

With *nitrites*, deep blue violet, the edges becoming red. Adding alcohol gave a red color.

With chlorates the resorcin reagent gave unsatisfactory results. Replacplacing it by beta naphthol gave a dull green, changing slowly to black. Alcohol gave a grayish or blackish solution.

Standard Alkalimetric and Acidimetric Solutions. North and Blakey (*J. S. C. I.*, XXIV., 395). Allusion is made to the various methods proposed and used by different analysts with references. Preference is given to the use of $NaHCO_3$ or $Na_2CO_3NaHCO_3$, when ignited, or even heated to 170° C., affords some NaOH, as has been proved by titration with phenolphthalein and methyl orange indicators, as also by the $AgNO_3$ indicator. $NaHCO_3$ in presence of moisture slowly dissociates, affording some Na_2CO_3.

The common impurity, NaCl, can be readily removed by washing. Pure $NaHCO_3$ when perfectly dry does not alter, and is not hygroscopic.

To prepare a salt absolutely pure for exact standardization the following method was used:

About 400 gms. of $NaHCO_3$ were washed in a large funnel with distilled water until all NaCl was removed; after drying in air on porous plates, and pulverizing, the material in rather thin layer was exposed under a bell jar to a moist atmosphere of CO_2 for several hours, until it gave no color with phenolphthalein. The mass was then dried in a desiccator over H_2SO_4, or better in a vacuum desiccator over P_2O_5.

When perfectly dry it may be kept in a well stoppered bottle for use and weighed out as $NaHCO_3$ for purposes of standardization, the errors due to ignition being thus avoided. It is well to allow a weighed quantity to stand over night in a desiccator (H_2SO_4) before using.

Ammonia in Waters. Trillat and Turchet (*C. Rend.*, CXL, 374). The method is based on the formation of NI_3 when KI and an alkaline hypochlorite are added to an ammoniacal solution. The NI_3 has an intense blackish color, and colorimetric comparison can be made in Nessler tubes. The test is made by adding to 20 or 30 c.c. of the water (or distillate) 3 drops of a 10 per cent. solution of KI, and 2 drops of a concentrated alkaline hypochlorite solution. (The authors used "Eau de Javelle.") Too great an excess of the hypochlorite will dissolve the NI_3. The results are compared with that obtained with standard NH_3 solution.

Magnesia in Limestones. Koppeochaar (*Fres. Zts. Anal. Chem.*, XLIV., 184). In the sugar industry, the presence of MgO in the lime used is especially objectionable, since much of the MgO passes into the sugar liquors. Consequently the determination of MgO in a limestone to be causticized for this purpose is the only determination required. In presence of the large amounts of CaO usually present, the CaC_2O_4 precipitate is likely to retain more or less MgC_2O_4 by the usual methods of analysis.

The author finds that if a large amount of the sample is dissolved in but little HCl, and the major part of the CaO precipitated out as $CaSO_4$ so little CaO remains that it can be separated by $(NH_4)_2C_2O_4$ without carrying appreciable amounts of MgO with it. He recommends to treat 50 gms. of the sample with 500 c.c. of dilute HCl, containing 37.5 gms. actual HCl, and after solution to mix it slowly with stirring with 50 c.c. pure conc. H_2SO_4. Stir frequently and place in a cooling mixture. Filter on a Büchner filter, after it settles clear (which should occur in about fifteen minutes), and render alkaline with NH_4OH, add 5 gms. $(NH_4)_2C_2O_4$ — filter, and in the filtrate precipitate Mg as phosphate in the usual manner, using 4 gms. Na_2HPO_4. Under these conditions the precipitate may be filtered in half an hour.

Qualitative for Ferrous Compounds. Blum (*Zts. Anal. Chem.*, XLIV., 10). Mix the solution with an equal volume of conc. H_2SO_4 cool, and drop in a crystal of KNO_3. If ferrous compounds are present, reddish or brownish streaks are seen about the crystal.

Alumina Precipitation. Divine (*J. S. C. I.*, XXIV., 11). Addition of a small amount of tannic acid (2 c.c. of a 2 5 per cent. solution to a solution containing 0.1 gm. Al_2O_3) permits $Al_2(OH)_6$ to be precipitated by NH_4OH in a form which filters and washes easily. Similar action does not occur with pure $Fe_2(OH)_6$. The tannic acid does not interfere with the subsequent separations of CaO and MgO.

Chromium in Steel. Ibbotson and Howden (*Chem. News*, XC., 320). When soluble in HNO_3 dissolve in that acid using as little as possible, expel nitrous fumes, dilute largely, and add 2 to 3 gms. $(NH_4)_2S_2O_7$ together with about 0.01 gm. $AgNO_3$. Heat until gas begins to evolve — then allow to stand a few minutes until Cr and Mn have oxidized to chromate and permanganate. (If much Mn is present, formation of MnO_2 may ensue which must be filtered off.) Cool the solution, add large excess of $NH_4C_2H_3O_2$ and then enough $Pb(C_2H_3O_2)_2$ to separate all Cr as $PbCrO_4$. Filter off, wash with dilute $NH_4C_2H_3O_2$, dissolve in HNO_3(Gr. 1.2) and determine Cr by use of excess of standard $FeSO_4$, titrating back the excess by standard permanganate.

If much W is present in the steel, it will not readily dissolve in HNO_3. Treat 0.5 gm. first with 10 c.c. dilute H_2SO_4(1 : 4) and boil. When decomposition is nearly complete — add 2 c.c. strong HNO_3, boil out nitrous fumes, dilute to 100 c.c., and to the solution (now cloudy with WO_3) add 20 c.c. HNO_3(Gr. 1 2) and about 0.04 gm. $AgNO_3$ and then 2 or 3 gms. $(NH_4)_2S_2O_7$. Heat, but do not boil, until the evolution of gas is completed. Cool dilute, and titrate as before.

Manganese in Slags. Namias (*Monit. Sci.*, XIX., 279). Two gms. of the slag are fused with alkaline carbonate, and SiO_2 separated in the usual manner by evaporation with HCl. The filtrate from SiO_2 is divided in halves. In one half the iron, alumina and manganese oxides are precipitated all together by use of NH_4OH, the filtrate being used for determination of CaO and MgO. In the other half, addition of cream of ZnO, precipitates only iron and alumnia, leaving Mn in solution. The precipitate (containing excess of ZnO), must be redissolved, and reprecipitated with NH_4OH. In presence of sufficient NH_4Cl, with decided excess of NH_4OH, contamination of the precipitate by ZnO may be avoided. It is perhaps safer to redissolve and reprecipitate again before weighing. Mn may be determined by titration with permanganate in the filtrate from ZnO precipitation.

Cobalt Electrolytically. Perkin and Prebble (*Ch. News*, XC., 307). Addition of hypophosphite afforded bright metallic deposits, but the results were too high — found to be due to deposition of some phosphide. Ammonium oxalate or tartrate afforded bright deposits with difficulty. With a low C.D. until the most of the metal was deposited, sometimes bright deposits were obtained. The results were high, apparently from presence of carbon. Use of ammonium borate gave much better results, but the appearance of the coating was bad, and in other respects that method was unsatisfactory for analytical work.

The most satisfactory results were obtained by adding to the Co solution (containing about 0.15 gm. Co) about 5 c.c. of a 5 per cent. solution of phosphoric acid, followed by 25 c.c. of a 10 per cent. solution of $(NH_4)_2HPO_4$ or of Na_2HPO_4, diluting to 130 c.c. and electrolyzing at 0.2 to 1 amp. 2 to 4 volts. After about half an hour, a deposit will appear on the anode which dissolves off quickly if a few drops of hydroxylamine sulphate are added. The phosphoric acid is used to prevent the formation of an insoluble Co phosphate, which tends to form also if the temperature is made too high (much over 60° C.). Much phosphoric acid caused the deposition to be slow.

Three to four hours sufficed for the precipitation of all the Co.

Experiments with the same additions for the deposition of Ni showed showed no advantage for that metal over the usual mode of electrolyzing the ammoniacal sulphate.

Copper, Zinc and Nickel, German Silver, etc. Fairlie (*Eng. Min. Jour.*, July 7, 1904). Dissolve in HNO_3, neutralize with NH_4OH and then render barely acid with H_2SO_4. Heat to 90° and add 10 c.c. SO_2 solution and 2 gms. NH_4CNS, which removes Cu. Settle, filter and add NH_4OH to the filtrate, then acidifying slightly with formic acid (or citric) and pass H_2S which separates Zn. Boil the filtrate with HNO_3, filter off free S, add NH_4OH and the AgI indicator and titrate the Ni with KCy.

Copper, Electrolytic Determination. Kufferath (*Zts. Angew. Chem.*, XVIII., 1785). The addition of a little formalin will prevent any co-precipitation of Ni, Co, Fe, etc. A platinum dish, the surface of which has been "matted" by rubbing with powdered glass is recommended. To the solution about (130 c.c.) is added 1.5 to 2 c.c. of formalin, the temperature is raised to 60° or 65° C. and a current of 2.5–3 amperes at 2 volts is passed. Two to two and one half hours suffice for complete deposition. HNO_3 or NH_4NO_3, also chlorides, should not be present.

Bismuth by Molybdate Precipitation. Miller and Cruser (*J. Am. Chem. Soc.*, XXVII., 116). A series of experiments were made to test the gravimetric method of precipitating Bi by $(NH_4)_2MoO_4$, igniting and weighing the precipitate in the form of Bi_2O_3, $4MoO_3$.

Correct results were obtained by proceeding in this manner: Add to the nitrate solution four or five times as much $(NH_4)_2MoO_4$ solution (the usual molybdate reagent containing HNO_3) as will suffice to combine with all the Bi. Then add a few drops of congo red, and run in very dilute ammonia from a burette until the solution becomes pink, then a few drops of HNO_3 until it takes a lilac shade, dilute to 150 to 200 c.c. and heat slowly up to about 60° C.

Then filter through a platinum Gooch crucible, and wash with a 3 per cent. solution of NH_4NO_3, until the bulk of the filtrate is 300 to 400 c.c. Dry at 160° C., moisten with a few drops of conc. HNO_3 and heat to barely dull red. Repeat, moistening with HNO_3 and ignition, then weigh. Repeat until the color is light yellow and the weight is constant. $NHNO_3$ was found to be preferable to $(NH_4)_2SO_4$ for washing. The temperature for ignition should not be above a dull red.

Separation of Silver from Lead. Lidhohn (*Ber.*, XXXVIII., 566). Dissolve the alloy or mineral in the usual manner with addition of tartaric acid, filter, neutralize and add $NaC_2H_3O_2$. Heat to boiling. Then add at least 2 c.c. of a 4 per cent. solution of hydroquinone for every 0.1 gm. Ag supposed to be present. Metallic Ag separates at once, Pb remaining in solution. Allow to settle out, and filter; wash with dilute NH_4NO_3 to facilitate filtration. Bi, if present, will be partially with the Ag.

Silver in Commercial Zinc. Friedrich (*Zts. Angew. Chem.*, XVII., 1636). Treat 200 to 1,000 gms. of the granulated sample with HCl until practically all is dissolved. Collect and wash the residue, melt up with 7.5 to 15 gms. test lead, and a little borax, and cupel the button in the usual manner.

Qualitative for Rhodium. Alvarez (*Chem. News*, XCI., 216). To a dilute solution of a Rh salt, add excess of NaOH in the cold to obtain an alkaline solution of $R/_2(OH)_8H_2O$ and pass into it "euchlorine" (generated by action of conc. HCl on $KClO_8$ in the cold). The solution first becomes reddish yellow changing to red which becomes more intense, darkens, and begins to cloud with a greenish precipitate, if the gas is still passed in. Finally the precipitate dissolves and the solution becomes blue, resembling in color that of ammoniacal copper solution, due to perrhodate Na_2RhO_4. This solution is bleached to yellow by SO_2, or on the other hand decolorizes giving a copious effervescence of O on addition of Na_2O_2 or persulphate. Chloroform, ether or benzene do not dissolve this compound. Pure aniline becomes red by contact with the blue solution, which is thereupon decolorized.

Tungsten. V. Knorre (*Ber.*, XXXVIII., 783). Benzidinchlorhydrate precipitates a white amorphous flocculent precipitate of benzidin tungstate. Precipitated in the cold, the filtration is slow, and on washing with water the precipitate is apt to run through. If precipitated hot, the mixture must be allowed to cool before filtering, as the precipitate is perceptibly soluble in hot solutions but it comes more dense and is more rapidly filtered. The better method is to add (in the cold) dilute H_2SO_4 or alkaline sulphate before introducing the benzidin hydrochlorate. The precipitate will then consist of the tungstate surrounded by the crystalline sulphate, which is easily filtered. Wash with dilute benzidin hydrochlorate. Ignition of the precipitate affords WO_8 for weighing.

Vanadium.— Separation from Cr, Fe and Al. Glasman (*J. Soc. Phys. Chim. Russ.*, XXXVI., 314). Add KI then H_2SO_4 and heat for twenty minutes. The I separated is redissolved by addition of SO_2. Then add a mixture of KI (20 per cent.) and KIO_3 (7 per cent.). Heat for half an hour on the water bath. $Fe_2(OH)_6$, $Cr_2(OH)_6$ and $Al_2(OH)_6$ precipitate completely. The I which is co-precipitated is brought into solution by means of $Na_2S_2O_3$, and the precipitate is washed. Evaporate the filtrate and washings to dryness with H_2SO_4 to expel I compounds, add HNO_3 to oxidize the Vd to V_2O_5 and then evaporate again with H_2SO_4 to expel HNO_3. Dissolve in water acidulated with H_2SO_4 add SO_2 to obtain V_2O_4. Boil out excess of SO_2, assisting the process by passing CO_2, and finally titrate with standard permanganate. 2 mols. $KMnO_2$ correspond to $5V_2O_5$.

Selenium Determinations. Gutbier. Metzner and Lohmann (*Zts. Anorg. Chem.*, XL., 291). An examination was made of the various methods of determining Se by reduction to elemental form. In all cases, boiling with the reducing agent was found to be necessary, and after reduction appeared to be complete, one needed to add more of the reagent, and boil again for ten minutes. Hydrazine hydrate gave good results only when the solution of SeO_2 was concentrated. Hydrazine hydrochloride was much better, and the need for concentration was not so marked. Hydrazine sulphate when HCl was added, worked well. SO_2 with HCl worked well, but large quantities of the reagents were required. Hydroxylamine hydrochloride requires prolonged boiling. In all cases where alkaline compounds were in the solutions (alkaline sulphites KI, etc.), some alkali was obstinately retained in the precipitate.

Perchlorates in Commercial Nitrate, etc. Dittrich and Bollenbach (*Ber.*, XXXVIII, 751). Place a layer of pure $NaNO_2$ free from Cl in the bottom of a large platinum or nickel crucible. On top of this place a weighed quantity of the sample taking care not to allow it to lie close to the sides of the crucible. Cover with another layer of $NaNO_2$ (using in all about 6 gms.) and heat up cautiously. After it fuses keep it in liquid condition for about 30 minutes, cool, extract with warm water, add $AgNO_3$, acidify with HNO_3 boil out all N_2O_5 and determine the AgCl in the usual manner.

Heating the nitrate itself, without use of $NaNO_2$ will also serve to reduce the perchlorate to chloride, but the temperature of the melt needs to be much higher to effect the change, a temperature at which there is danger of volatilization of alkaline chloride.

Small Amounts of Bromine and Chlorine in Commercial Iodine. Tatlock and Thompson (*J. S. C. I.*, XXIV., 187). To 5 to 10 gms. of the sample add ten times its weight of water, and then introduce Zn as dust or finely granulated in small quantities at a time, to avoid any sensible rise in temperature. When all I has been dissolved, filter, wash a few times, and to the solution add 3.5 to 7 gms pure $NaNO_2$. Then acidify carefully with dilute H_2SO_4 when all I is liberated—the major portion in solid form. Filter off, wash a few times with cold water, and from the filtrate separate the remaining I by shaking in a separator funnel with benzene. Test the aqueous solution with $NaNO_2$ and H_2SO_4 to ensure the complete removal of I. (CS_2 or $CHCl_3$ may be used in place of the benzene.) From the solution precipitate Br and Cl by $AgNO_3$ with a little HNO_3 and boiling. To remove AgCl from the precipitate, use a solution consisting of 90 c.c. water, 10 c.c. NH_4OH of sp. gr. 0.88 and 2 gms. $AgNO_3$. Pour backward and forward about 50 c.c. of this solution through the filter, and wash finally with the remaining 40 c.c. AgBr is left undissolved which should be washed with dilute HNO_3 and then with hot water. In the ammoniacal filtrate the AgCl may be separated for determination by acidifying with HNO_3 and warming. After drying and weighing the precipitates should be tested for their purity.

Carbonic Acid in Natural Waters. Winkler (*Zts. f. Anal. Chem.*, XLII., 735). Passing H through the waters carried off the CO_2 with it. The CO_2 may be absorbed in a weighed amount of KOH solution. In sulphur waters H_2S may be taken out in the same manner by use of CO_2.

Carbon Dioxide and Chlorine in Gaseous Mixture. Schlötter (*Zts. Angew. Chem.*, XVII., 301). 100 c.c. of the mixed gases is run into a Bunte burette. (The use of 20 to 25 c.c. of water to establish the correct level does not cause appreciable error.) Hydrazine sulphate is then introduced. After shaking, add a little more of that reagent, shake again, and after proper adjustment read off the diminution in volume. The reaction being $N_2H_4 + 2Cl_2 = 4HCl + N_2$, double the decrease in volume gives the volume of the Cl. The CO_2 may then be determined in the usual manner by absorption with KOH.

Carbon and Phosphorus in Steel. Report of Committee (*Trans. Am. Inst. Min. Eng. Bi-monthly Bull.*, March, 1905, p. 289) The methods used, and the results obtained are given and discussed by the analysts:

Baron Jüptner (Austria), A. A. Blair (U. S.), G. Dillner (Sweden), and J. E. Stead (England). For carbon, Jüptner and Blair decompose the sample with $CuCl_2$,2KCl and separate the C by filtration. The first uses CrO_3 "wet combustion"; the latter uses the "dry combustion"; Dillner decomposes with $CuSO_4$ and conducts the whole operation of combustion (by CrO_3) in the same flask, passing all evolved gases through a hot platinum tube; Stead burns the carbon directly in the steel in a current of oxygen, inserting the sample in the combustion tube, without previous treatment to separate any part of the Fe.

For P weighing the "yellow precipitate" is used by all except Blair, who uses the Emmerton titration method.

Silicon by Drown's Method. Thill (*Zts. Anal. Chem.* XLIII., 552). Addition of NH_4Cl permits the application of naked heat without bumping and spurting of the solution on evaporating and thus permits the hastening of the operation.

Ferrosilicon. Lucchese (*Ann. Chim. Anal.*, IX., 450). Mix 1 gm. with 2 gms. dry Na_2CO_3 and 2 gms. Na_2O_2 in a platinum crucible. Heat gently for 5 minutes then holding the crucible in the tongs, and giving the contents a rotary motion, heat for 15 minutes to dull red. Turn out while still fused, dissolve in water and acid, and separate SiO_2 by the usual methods.

Phosphorus in Iron Ores. Rowland and Davies (*J. S. C. I*, XXIII., 1186). The ore is well mixed with its own weight (or less) of calcined MgO and incinerated at bright red heat for an hour. Then treatment with HNO_3 and boiling for 10 minutes, will bring all P_2O_5 into solution. From this solution P_2O_5 may be separated by molybdate mixture, and the amount determined by titration with standard NaOH (Handy's method, vide *J. Ann. and App. Chem.*, VII., 204).

Colorimetric for Phosphorus. Hewitt (*J. Am. Chem. Soc.*, XXVII., 121). The "yellow precipitate" obtained with molybdate is dissolved in N/10 NaOH, H_2S passed in, and the colors compared with those obtained from standard solutions. The standard solution is made by dissolving 0.2737 gm. of yellow precipitate in N/10 NaOH, adding half as much more than is just necessary to dissolve, and making up to 500 c.c., 10 c.c. = 0.000009122 gm. P. Pass H_2S 5 minutes, immerse in boiling water 5 minutes and then read in Nessler tubes.

Sulphurous Acid. Pinnov (*Zts. Anal. Chem.*, XLIII., 91). Titration with standard permanganate affords incorrect results because a portion of the SO_2 is converted to dithionate.

Volumetric for Sulphates, etc. Andrews (*Am. Chem. Journ.*, XXXII., 476). The author describes a method (*Am. Chem. Jour., XI.*, 567), consisting in adding a solution of $BaCrO_4$ in HCl, then neutralizing, which precipitated both $BaSO_4$ and excess of $BaCrO_4$. On filtering CrO_3 corresponding to the SO_3 present, remained in the solution, and was determined iodometrically. The keeping quality of the HCl solution of $BaCrO_4$ has been found to be poor. Substitution of trichloracetic acid for HCl, proved to be entirely satisfactory.

Sulphate Determinations. Pattinson (*J. S. C. I.*, XXIV., 7).

An examination of Lunge's method for determining S in pyrites with

especial reference to the precipitation of basic ferric sulphate along with the $Fe_2(OH)_6$ by ammonia. Precipitation in the cold with about 5 c.c. excess of ammonia gave the best results in this respect, the tendency to formation of basic sulphate apparently increasing with the temperature. The presence of NH_4Cl has but little effect in increasing the solubility of $BaSO_4$. An excess of 1 to 2 c.c. of HCl in 300 c.c. of solution is quite permissible. Dr. Lunge's conclusions as to the influence of the temperature are not in accord with the above observations.

A note is appended as to two possible sources of error in S determinations: One, the presence of sulphates in the red rubber corks frequently used in the wash bottles; the other the occurrence in some $BaCl_2$ of sulphur compounds (resulting from manufacture from mineral barite) which under the conditions produced may oxidize up, and increase the amount of $BaSO_4$ found.

Sulphur in Ores, Limestones, etc. Hartwigsson (*Chem. Zt. Rep.* XXIX., 4).

The author has found that many ores, etc., when heated in a current of H, either give off S in the form of H_2S, or the element is converted to sulphide in such combination that H_2S is evolved on treatment with HCl. The material is placed in a porcelain boat which is slid into a combustion tube. Through this tube a current of H is passed,—when the air has been expelled the temperature is raised to a red heat, the issuing gases being passed through (acetic) acid solution of Cd $(C_2H_3O_2)_2$ contained in two Erlenmeyer flasks. After heating the material for 45 to 60 minutes in this manner, the tube is cooled and the material placed in an evolution flask, and the remaining H_2S set free by treatment with HCl, the escaping gases being passed through the same Cd solution.

The solution now contains the S in form of CdS. Add excess of standard I solution, and then 10 to 20 c.c. HCl and titrate with standard thiosulphate to determine the excess of I over that required to react with the H_2S liberated.

Sulphur in Coal by the Eschka Method. Bender (*Zts. Angew. Chem.*, XVIII., 293). In Westphalia the Eschka process is conducted in a tube of hard glass (2.8 to 3 cm. diameter) held by a clamp in a horizontal position. The tube is sealed at one end so that it resembles an ordinary test tube in appearance. The mixture of coal MgO and Na_2CO_3 is charged in, and then shaken so that when horizontal there is an air space above the mixture. The charged tube is first thoroughly dried in an air bath, and set in the clamp while still hot. Then the heat of a burner is applied — at first at the edges of the mass, finally to the main portion. When the heating is terminated, the tube is set in a slanting position over a porcelain dish. As it cools its end usually cracks off and falls into the dish. The remainder of the operation is conducted in the usual manner.

Nitrogen in Iron and Steel. Braune (*Oesterr. Zts. Berg. Hutt.*, LII., 491). Dissolve 1 gm. in 10 c.c. of HCl (Gr. 1.124) free from NH_3. Run the solution into a flask containing 250 c.c. of boiling water, containing sufficient NaOH to neutralize all free acid, and "Nesslerize" the distillate.

Nitrogen as Nitrites. Weston (*J. Am. Chem. Soc.*, XXVII., 281). A comparison was made of the methods of applying the naphthylamine

test, the Griess-Warrington (using HCl) and the Ilosvay (using acetic acid). The conclusions were: HCl in excess interferes with the delicacy of the reaction, while $HC_2H_3O_2$ does not. The speed of the reaction varies with the amount of HCl, and in some degree with excess of the reagents. Ilosvay's method is more rapid. The various modifications produce apparently no variation in the tint obtained. Thorough mixing is, however, necessary.

Nitrates. Gutbier (*Zts. Angew. Chem.*, XVIII., 494). The author has examined the application of "nitron" the reagent of M. Busch for the valuation of commercial nitrates. The reagent (called for convenience "nitron") is diphenylen-anilo-dihydro-triazol ($C_{20}H_{16}N_4$) which forms an exceedingly insoluble compound with HNO_3 which can be filtered off and weighed. The method used consists in dissolving 0.1 to 0.15 KNO_3 (or a corresponding amount of any other nitrate) in 80 c.c. of water in a covered beaker, adding 12 to 15 drops of dilute H_2SO_4 and heating to incipient boiling. Remove the heat, and add 12 to 15 c.c. of a 10 per cent. solution of "nitron" in 5 per cent. acetic acid. Stir well, and allow to stand for about half an hour or more. When the mixture has taken the room temperature, stand for 1 to 1½ hours in ice water, then pour mother liquor and precipitate upon a weighed Gooch or Neubauer filter, suck dry, then wash by repeated application of small amounts of ice water, using about 1 c.c. at a time. In this way 10 or 12 c.c. of water can be made to suffice, the suction being kept weak throughout. Then dry at 105 to 110° to constant weight (which the author found required about 45 minutes). The test analyses showed excellent results. Under the conditions described, the precipitate is very crystalline, and consists of $C_{20}H_{16}N_4.HNO_3$.

Portland Cement. Russian Standards (per *J. S. C. I.*, XXIV., 91). The ratio of CaO and alkalies to SiO_2, Al_2O_3 and Fe_2O_3 should be not less than 1.7 or more than 2.2: SO_3 not over 1.75 per cent.; MgO not over 3 per cent.; foreign substances not over 2 per cent. Tests to be made at temperature of 16° to 18° C. Sp. gr. after drying at 120° C. must not be less than 3.05.

Hardening when gauged must not begin sooner than 15 minutes and must not be complete sooner than 1 hour, or later than 12 hours. The Vicat needle is used. Blow cracks or warping must not appear on warming or standing in water for 27 days. In the hot test heat to 120° C. for 1½ hours, 24 hours after setting.

The fineness of grinding must be such that not more than 50 per cent. of residue shall be left on a sieve of 4,900 meshes (0.05 mm. wire) per sq. cm., or more than 15 per cent. on a 900-mesh sieve of 0.1 mm. wire. Test blocks to have a sectional area of 5 sq. cm. at point of rupture. With cement gauged neat, the minimum tensile strength of these blocks is fixed at 20 kilos at the end of 7 days, and 25 kilos at the end of 28 days, except that if the first test shows 23 kilos the second test is omitted. For cement sand mixtures, the normal sand is quartz sand sieved on sieves with 64, 144 and 225 meshes per sq. cm. (wire 0.4, 0.3 and 0.2 mm. respectively). The residues left on the 144 and 225 sieves shall be used as "normal sand." The maker's name and year of manufacture must be marked on the casks. Delivery in bags is only allowed by special consent.

BOOK REVIEWS.

The Steam Turbine. By Dr. A. STODOLA, of Zurich. Translated by DR. L. C. LOWENSTEIN. New York, D. Van Nostrand Company, 1905.

No problem of steam engineering ever given the mechanical engineer for practical solution has called for more earnest study from the double standpoint of hypothetical possibility and practical limits of execution than the design and building of steam turbines.

It is probably equally true that no problem of this class has been so long before the scientists and engineers of the world with so little tangible results of a clear, definite, quantitative kind. Practically every thing that is known of any importance has been worked out during the last ten years. During this time the work of development has been taken up by a continually increasing number of men of four distinct classes, equally eager for results. The first class, embracing the large number of dreamers or inventors, with no conception whatever of what has been done or might be done in this or similar steam engineering fields, has flooded the patent offices and the offices of anxious investors and promoters with endless useless schemes. The pure physicists, consisting the second class, have expended not a little effort in expounding hypotheses of heat transformation by free expansion with no useful effect. Following the class of purely hypothetical investigators with no knowledge of experimental measurements, comes the class of experimenters on turbine machines with no knowledge of the limits of hypothetical possibilities and totally ignorant of all contemporary data. This class is responsible for many commercial failures and the loss of considerable time and money.

By experiment, combined with theoretic computations on flow of steam through nozzle, the reception of the jet by buckets, the friction of steam on metal surfaces, the stresses and forces in hot wheels at high rotative speeds data can be secured to establish or disprove various theories and this data is essential for design. This, the most fruitful field of work, is occupied by a class smaller in numbers than any of the rest, probably not more than a dozen men, at the head and front of whom is Professor Stodola, the author of this work.

The book contains for most men a mine of material of both kinds, hypothetical and experimental on every question basic to the general turbine problem. The presentation is sane, rational and timely and will be a most valuable check on the dreamer, the theorist and the builder. The builder is probably the most directly concerned, for as the translator, Dr. Loewenstein truly says: "There is no branch of machine design in which a complete knowledge of the theory involved is so necessary as in turbine design." But this theory or hypothesis must be the correct one, supported, not contradicted by experimental observation.

That this book does contain some of the commonly accepted but unsupported hypotheses does not detract from its value, because of the newness of the material and the necessity for at least a working hypothesis which, in such cases, is better than none at all.

The book opens with a mathematical statement of the equivalence of work done by balanced expansion and kinetic energy of the jet by free expansion, from which statement an expression for velocity of a jet is derived.

Following this (pages 14 to 42) the transformation of jet velocity is treated for single and multiple stage impulse and reaction turbines with factors representing reduction of velocity from nozzle and bucket friction and eddy currents. Steam flows, steam friction, and steam shock are treated next from both the hypothetic and experimental standpoint, together with pressure changes in straight tubes diverging and converging nozzles for varying conditions. This is given in forty-three pages after which some experiments on turbine bucket impact are reported.

By the same methods used for jet determinations, the energy changes and thermodynamic efficiency receives a thirty-eight page treatment almost entirely hypothetical, followed by a very valuable ten page report on some experiments on the friction of rotating discs in steam.

The third part of the work (pages 141 to 214) is concerned entirely with form of the turbine parts and their design through analysis of stresses. Types of turbines with the growth of new ideas and a little data on performances makes up Part 4 (pages 214 to 322).

The last part of the work is concerned with what is almost entirely a study of hypotheses on the distribution of pressure in a cross section of a jet or in a stream passing a turbine bucket. Changes of form in high speed discs and shafts due to kinetic, thermal and static stresses, vibrations and frame resonance.

To this rather satisfactory book is added an appendix on the future of the heat engine not by any means so satisfactory as it is entirely speculative and weakens rather than strengthens the book.

CHARLES E. LUCKE.

The Steam Engine and Other Steam Motors, Volume I. By Prof. R. C. H. HECK, of Lehigh University. New York, D. Van Nostrand Company.

Steam engines have been in use for so many years that all the involved problems are now pretty well understood. The questions of basic principles, variations of form to meet conditions, refinements of design or regulation, long life and light weight in reciprocating steam engines have all these years been the subject matter of innumerable papers and books.

The modern steam problems are confined almost entirely to the use of steam in turbines and the relation of the auxiliaries and materials to the plant as a whole.

This book of Professor Heck's makes no attempt to treat the modern problems or to assist in their solution. It is rather an arrangement of some of the material of the older kind, primarily for the use of students and the form is dictated by the experience of Professor Heck with students at Lehigh University.

The first 136 pages give the basic principles of heat conversion into work as carried out in the cylinders. This treatment thermodynamic and experimentally is fairly good and should serve to correct the many peculiarly false ideas of the average student. No new matter is here introduced over what has been before presented in books like that by Perry, and compared with the work of Perry there are not a few omissions. When not used in cylinders, steam may do work in turbine

engines by free expansion. The heat conversion part of the turbine engine is the nozzle and in pages 137 to 208 the author gives some of the generally accepted data on jet work such as may be be found in the books of Kennedy and Stodola. Following a twenty-four page presentation of the ordinary use of entropy diagrams to the steam work problem, Professor Heck takes up the question of the principal forces in the engine giving the rest of the book, 132 pages, to this subject. This treatment of forces in the principal engine parts due to steam pressure and inertia is rather more fully treated than is usual in most other books on the steam engine and is by far the best thing in the book. The length of this treatment is no doubt due to the extraordinary difficulty of the average student with this subject and is justifiable on these grounds.

The works of Professors Klein and Le Conte are the usual references for this question of force distribution in the engine and contain all essential data. In cases where the whole subject of the steam engine must be treated in a short time and in one book this work will undoubtedly be useful in most of the technical schools, however, it has been customary to use several books, each treating quite completely one phase of the subject. This will probably continue to be the case, as it enables the student on leaving to carry away for future reference a set of books with which he has become familiar and which contain much more detailed information of the kind he needs in his work, than could possibly be condensed into one book. CHARLES E. LUCKE.

Text-book of Organic Chemistry. By HENRY LEFFMANN, A.M., M.D., and CHARLES H. LAWALL, Ph.G. Philadelphia, P. Blakiston's Son & Co., 1904. Pp. ix + 215. Price, $1.00.

The first 40 pages have to do with the "Principles" such as structure and classification, isomerism, organic radicles, homologous series, etc. "Descriptive Chemistry" follows with 137 pages on aliphatic and cyclic compounds and 30 pages devoted to alkaloids, proteids, and enzymes. Particular attention is given to those compounds of interest to the pharmacist and the physician.

The best that can be said of this book is that the press work is good. In other respects it is a shining example of what a text-book on organic chemistry should not be. There is little logic in its arrangement. Such topics as the relationships of organic compounds, general methods of preparation, and the typical chemical properties of the various groups are notable by their absence. The book abounds in involved, misleading, and absolutely incorrect statements. We are told that "*cyanogen*, H — C ≡ N" and "iso*cyanogen*, C ≡ N — H" (italics are ours) are illustrations of true isomerism; that butane is commonly known as Cymogene, pentane as Rhigolene and hexane as Gasolene; that cyclopropane is isomeric with propane; that propionic acid is a crystalline solid. A structural formula for Salicin is given on page 113 that bears no resemblance to the correct one and that even does not agree with the empirical formula given on the previous page. The structural formula for saccharin (page 134) is wrong. On page 128 we find the structural formulas for the two possible tautomeric forms of phloroglucin and they indicate that the change from the enol to the keto form is by the migration of the three *oxygen* atoms. The examples given above are a few only of the many errors found in this remarkable book. V. J. C.

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